

ICOM COMMITTEE FOR CONSERVATION

9th Triennial Meeting
Dresden, German
Democratic Republic
26–31 August 1990

Preprints Volume II



COMITÉ DE L'ICOM POUR LA CONSERVATION





A NOTE ON THE COVER

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Finally, a word of appreciation goes to Janet Bridgland, Chairman of the Committee, and to the members of the Directory Board for initiating and supporting the changes realized in this edition.

—K.G.

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Working Group 13

Natural History Collections

Collections d'histoire naturelle



ABSTRACT

A method for determining the change of colour of birds feathers is described. Budgerigar feathers (*Melopsittacus undulatus*) were exposed to light with and without ultra-violet radiation. The changes in reflection spectra and colour (ΔE CIE) were measured. A fast initial change of colour followed by a much slower change was revealed. Radiation dose was assessed by blue wool fading standards. Standards 6 and 7 were shown to be unreliable when UV is excluded.

MELOPSITTAUS, FEATHER,
PIGMENT, FADING, LIGHT,
ULTRA-VIOLET, BLUE-WOOL
STANDARDS

FADING OF FEATHERS BY LIGHT

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Introduction

Feathers are the distinguishing features of birds. The colour of feathers are used by ornithologists for classifying species and breeds and by various societies for ornament.

Few studies have been carried out into the stability of feather coloration. Sir Sydney Harmer exposed four red feathers to sunlight through various glass filters at the British Museum (Natural History) in 1914. Unfortunately the results were not reported [1]. Lord Rayleigh reported the effect of high energy ultra-violet radiation on the iridescence of a peacock's feather [2]. Test showed that carotenoid pigments (yellow and red) from *Colaptes* spp. were more susceptible to fading than the melanins when exposed to weathering [3]. The mechanisms by which colours are produced in feathers fall into the two categories of structural effects and pigments, though the two mechanisms may be combined to achieve one colour. Structural effects cause interference (iridescent reflection) or scattering (blue reflection) of light. Pigments absorb light to produce a range of reflection colours. Considerable research has been carried out into the various physical structures and the pigments that result in coloration [4]. It is known from common observation that natural history materials fade and change colour on exposure to light and air. The recommendation that feathers be displayed at no more than 50 lux [5] appears to be the result of a conservative guess, rather than based on quantitative data. A method for studying fading has been developed using budgerigar (*Melopsittacus undulatus*) feathers which are widely available from cage birds. The pigments colourants in budgerigars have not been identified.

Method

Colour measuring instrument: John & Reilhofer reflection spectrophotometer ER10. The measuring head incorporates a xenon pulse illuminant with a 45/0 CIE geometry. Light reflected from a 10mm diameter spot is collected, split by a diffraction grating and measured by a diode array. A reference beam is measured simultaneously. The device is calibrated using a white gloss standard whose reflection characteristics are retained in the hardware and used in the calculation of the absolute reflection values. Colour values for CIE illuminant D65 with a 2 observer were extracted.

Sample presentation: Portions of feathers are stuck onto a black anodised aluminium sheet (49 x 114 x 0.5 mm) whose luminous reflection is 0.41. Double sided adhesive tape is applied down the sides of the sheet and the feathers span these. Sufficient layers of feathers are applied to obscure the black background. The measuring points are along the long axis of the sheet. Nicks are cut along the edges to enable the sheet to be replaced reproducibly in a measuring jig, figure 1. The spectrophotometer is supported on a tripod which is adjusted for the correct distance from the sample, figure 2. Presentation of blue wool samples is similar though only one layer is used. Previous experiments involved clamping the samples to the port of an integrating sphere. The distortion caused a greater change in the measured colour than that due to fading. The use of a xenon pulse (1/50 second) also eliminates the changes due to progressive heating by the beam of a scanning spectrophotometer (up to 3 minutes). The samples were measured in a room with no humidity control, contributing to the variability of the readings.

Fading apparatus: A Microscal (Mark 1) Light Fastness Tester is used with a Philips MBTL mercury discharge lamp and 12 type "A" water cooled cells. The sample cells are glazed and capped to form a moderately well sealed environment. To all the windows are applied 3mm Perspex (poly(methyl methacrylate)) sheet, half of these a UV absorbing grade (VA) "UV filtered", the remainder a

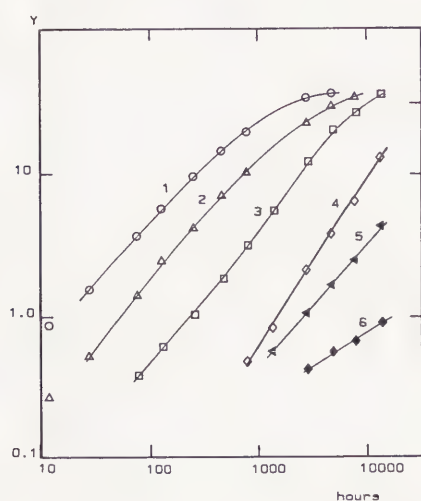


1. Feathers mounted on a black anodised aluminium sample sheet. The sheet has been nicked along one edge to provide reproducible alignment at six sampling positions when placed on the baseplate of the measuring jig.

3. Relative power received by the samples from the fading lamp.
with ultraviolet (VA)
filter, without.



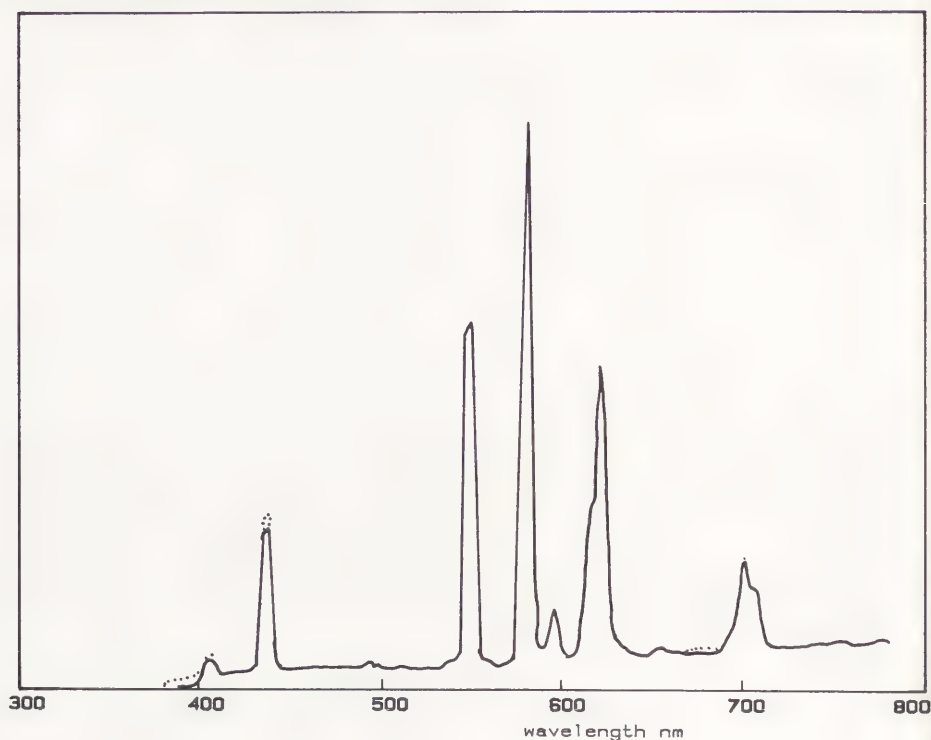
2. Measurement head of reflection spectrophotometer in position on measuring jig. The tripod legs of the jig are adjusted to ensure that the distance between the sample and the window of the spectrophotometer is correct. The legs drop into only one position on the baseplate. Connecting wires to the measuring head have been removed for clarity.



4. Fading of blue wool fading standards using MBTL lamp with clear Perspex filter, expressed as ΔY (change of luminous reflectance) against hours of exposure.

Standards 1 (o); 2 (Δ); 3 (\square); 4 (\diamond); 5 (\blacktriangle); 6 (\blacklozenge)

relative energy distribution



standard clear glazing grade "unfiltered". The radiation reaching the samples in these two arrangements is shown in figure 3. The illuminance received by the samples was 17,800 lux through VA filter (UV excluded) and 17,200 through the clear Perspex. The sample sheets in the cells are pressed against the cooled back plates by sprung holders. Humidity control is achieved using saturated sodium chloride solutions in each water cooled cell. The effective relative humidity was found to be in the mid 50s % RH using the Humidity Test Control [6], in line with the literature [7].

Calibration: Two sets of blue wool fading standards, 1 to 7, BS1006 [8] equivalent to ISO 105 [9], were applied to the black sample sheets as described above. Luminous reflection values (Y) of these standards are given in table 1. One of the sets were placed in a UV filtered cell, the other in an unfiltered cell. The sets were withdrawn from time to time and measured. In the light of work by Feller and Johnson-Feller [10], ΔY (change in luminous reflection) and ΔR (change of reflectance at maximum absorption) are equally useful in describing the fading of the blue dye. Figures 4 and 5 show the fading process in terms of ΔY as a function of time passed. The relationship of the standard grey scale with ΔY and ΔE is given in table 2. As an approximate guide, the eye can just detect a difference in colour if there is one unit of change in ΔE . Blue wool standards with poor light fastness are faded by both visible and UV radiation, while the more resistant materials are faded only by the shorter wavelength components of the incident radiation [11]. Figure 6 demonstrates the difference in behaviour of the standards with the two exposure conditions. Standard 1 is only marginally affected by the additional UV component, whereas standard 6 is far more sensitive to the amount of UV it receives. The UV component obviously accounts for the bulk of the fading of standard 6. Where fading is due entirely to visible light, standards 6 and 7 (not shown) become unreliable indicators of radiation received.

Colour evaluation: The colour system used is CIELAB [12]; L^* scale of light/darkness, a^* scale of red/green, b^* scale of yellow/blue-ness. For example when $L^*=80$, $a^*=0$, $b^*=0$, the colour is very light grey, and when $L^*=50$, $a^*=-30$, $b^*=30$ the colour is bright green. Various measures of colour difference are available [13] and none are totally satisfactory so the standard CIELAB ΔE , = $[(\Delta L)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, is used for comparison between samples.

Table 1

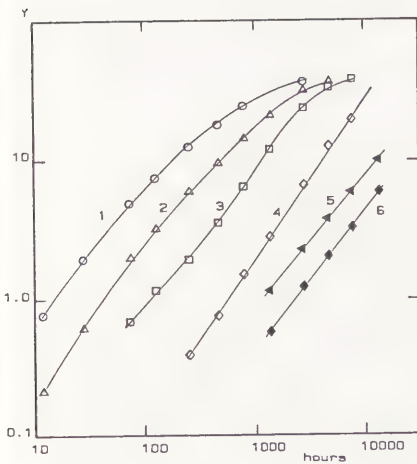
Blue wool fading standards, initial values of luminous reflection (Y CIE 2 observer D65)

Standard	Y UV filtered	Y unfiltered
1	8.04	8.13
2	9.31	9.11
3	9.26	9.33
4	6.56	6.50
5	4.83	4.79
6	6.21	6.36

Table 2.

Grey scale [8] expressed as ΔY and ΔE (CIELAB)

Grade	ΔY	ΔE
5	0	0
4	0.94	1.7
3	2.13	3.4
2	4.62	6.8
1	9.74	13.6



5. Fading of blue wool fading standards using MBTL lamp with UV absorbing Perspex filter, expressed as ΔY (change of luminous reflectance) against hours of exposure.

Standards 1 (o); 2 (Δ); 3 (□); 4 (◇); 5 (◄); 6 (◆).

Table 3. Colours of the budgerigar feathers used, in terms of CIELAB2 observer D65. The averages and sample standard deviations were derived from readings on all of the six replicates used for each colour.

Colour name	L*	b*	a*
grey-blue	49.02 ± 4.47	-3.97 ± 0.40	-5.06 ± 1.51
bright blue	57.67 ± 1.56	-21.51 ± 0.71	-22.64 ± 1.55
grey-green	60.05 ± 1.53	-2.99 ± 0.58	6.70 ± 0.57
bright blue	52.77 ± 1.57	-43.66 ± 1.18	35.15 ± 3.07

Budgerigar Feathers

Feathers were plucked from carcasses which had been frozen for up to nine months. Both body and wing feathers were used without further preparation. Four colours were chosen, see table 3 and figure 7. The greyish colours had very little pigmentation while the two bright colours were obviously highly pigmented. Two colours were applied to a sample sheet, and three measurements were taken of each colour on a sheet. Duplicate sample sets were made for exposure through VA and ordinary Perspex. Exposure produced similar effects for replicate samples within each group. Because of the variation between and within feathers, it is impossible to detect or measure changes of colour by comparing exposed/unexposed pairs to a visual grey scale. A purely instrumental method of measuring change is therefore employed.

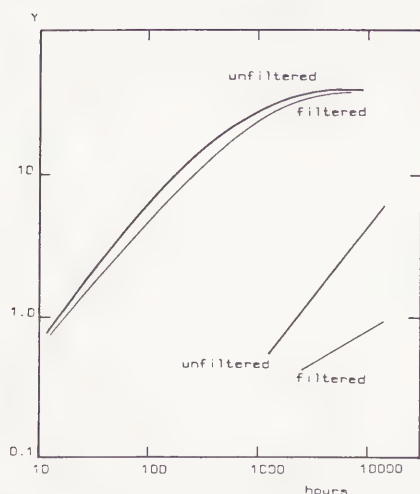
The feather colours showed two distinct types of behaviour during exposure to radiation, table 4. Simple progressive change of colour (increase in ΔE) was seen in only one feather, the grey-green, figures 8 and 9. The change in colour of the feather is compared with the changes (ΔE) seen in the blue wool standards in order to achieve an estimate of the stability of the colour. More complex changes were seen in the grey-blue and the bright colours. All of these suffered a rapid initial change in colour followed by a period of stability, and then the start of a further stage of fading. The initial change occurred quickly on exposure to UV but more slowly if that was eliminated, exemplified by the bright blue colour, figure 10. It is apparent from the changes in its reflection spectra, figure 11, that two processes (at least) are involved. First a yellow pigment with an absorption maximum around 400nm is bleached and subsequently undergoes further degradation. Much more slowly, a pigment absorbing around 680 nm is lost. The initial loss of absorption around 400nm was also seen with the grey-blue colour. The change in the grey-green reflectance, figure 9, includes this loss of absorption but the separate effect of this change may be masked by the overall bleaching of the colour. By contrast, the initial change in the bright green colour is due to a reduction in reflection around 520nm, figure 12.

Table 4. Fastness of budgerigar feathers on exposure to UV filtered and unfiltered light by comparison with blue wool fading standards.

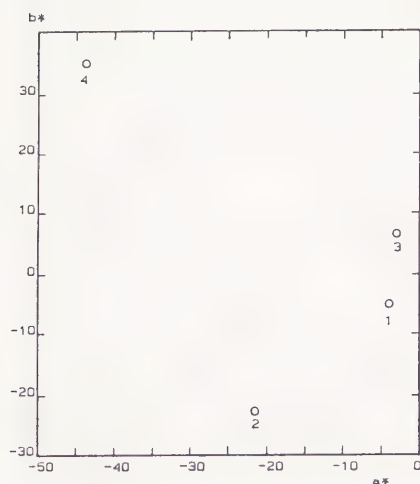
Feather colour	Fastness of colour [2] UV filtered	unfiltered	effect of UV [3]
grey-blue	<4, (<6)	IC, >7	no difference
bright blue	>3, (<6)	IC, >7	IC faster
grey-green	4	5	no difference
bright green	<4, (6)	IC, 6	fading faster

Notes

1. For definition of colours see table 2.
2. The fastness indicated is that of the blue wool fading standard whose fading curve most closely matches (by eye) that of the sample over the appropriate part of its curve. The sample curve is compared with those of the standards exposed in the same conditions. Where a specimen shows two different fading curves (see figure 10), this is indicated by two values. IC indicates that a sharp initial change occurred before repeat measurements began.
3. This column indicates whether including UV in the exposure conditions made any significant difference to the rate of change of colour. No difference was made to the type of change. "IC faster" means that UV speeded up the initial change, but subsequent change was not affected. "fading faster" means that UV speeded up all the fading processes.



6. Comparison between the behaviour of blue wool fading standards 1 and 6 exposed to UV filtered — and unfiltered radiation —



7. CIELAB (2 observer, D65) diagram showing the colours of the feathers before fading: grey-blue (1), bright blue (2), grey-green (3), bright green (4).

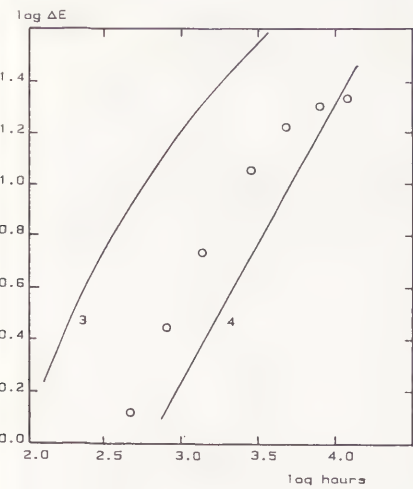
Conclusions

Blue wool standards: The blue wool standards are designed to assess the cumulative radiation dose in situations exposed to radiation comparable to daylight. For this purpose, they provide an easy and inexpensive method for evaluating the total dose. Considerable data exists on their behaviour under daylight [14], or simulated daylight such as xenon fading lamps, "daylight" fluorescent lamps [10], and a variety of other light sources [15]. All light sources have different spectral compositions so of each light source must be calibrated with the blue wool standards. However, when the radiation is no longer an approximation to UV containing daylight, it must be questioned whether the blue wool standards (especially 6 and above) provide a valid method of assessing the radiation dose.

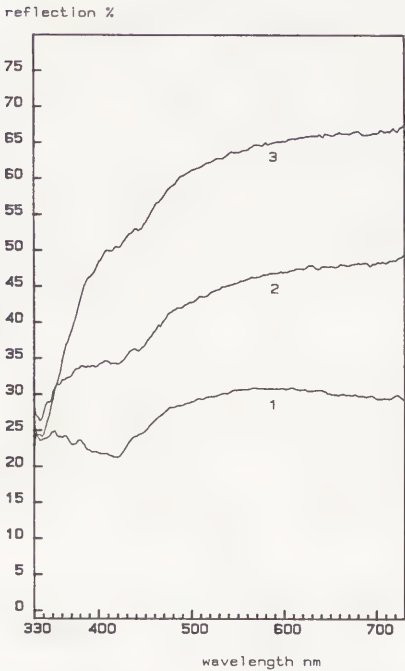
The accelerated light ageing conditions used here result in reproducible and consistent behaviour in the standards 1 to 5. The only significant difference caused by filtering out the UV is an increase in the time required to achieve a given fading of the standards. The slope of the curves remains the same. The shift of the UV filtered curves relative to the unfiltered increases steadily from 1 to 4, with the shifts of standards 4 and 5 being approximately equal, as the standards become less sensitive to visible light. Standards 6 and 7 fade very differently when UV radiation is filtered out and are not then reliable. For museums which ensure UV filtration for both daylight and artificial sources, only standards 1 to 5 should be used for monitoring integrated light exposure in displays and for testing purposes.

Budgerigars: Domestic budgerigars are descended from birds who lived in the arid central Australian scrubland exposed to very bright sunlight. The colours in domesticated birds will share the native characteristics, although accentuated. The wild bird is predominantly green and grey with yellow round the head and blue tail feathers. It is not surprising that the basic colours of green and blue are stable to exposure to both light and UV. A yellow pigment may be the colouring component of the grey-green feathers. If so, it appears surprisingly fugitive. Experiments with yellow feathers will be necessary to clarify this point. The black pigment, probably a melanin in small amounts in the grey-green feathers, also changes quickly. UV increases the rate of fading both in the short term and long (for bright green), providing further support for excluding UV from displays and storage.

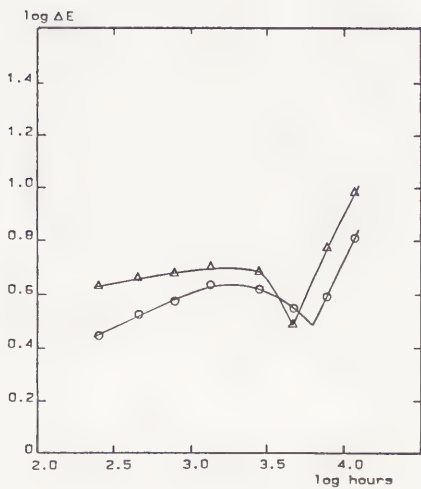
The feather colours show a rapid initial change on exposure. This behaviour is seen in other natural colouring materials such as dyed wools [16] and coloured wood [17]. All of these involve mixtures of colouring agents which add variety to the colour. Once the initial change has occurred, the colour will remain static. This may account for the criticism that museum displays are "drab and never change". They actually sparkled for the first few months then the interest literally faded. The display of coloured materials which have never been exposed to light must therefore be carefully considered. Suggestions have been made that, because temporary exhibitions cause short term exposure, higher light levels are permissible as the average cumulative exposure over years is still low. It may be that this initial exposure causes the bulk of the likely damage in a museum. By repeatedly choosing the most attractive objects for display in preference to those which were used previously, the stock of objects in near original condition will be eliminated. The acceleration in production of new and temporary displays during recent decades threatens to reduce the past to an incorrect drabness.



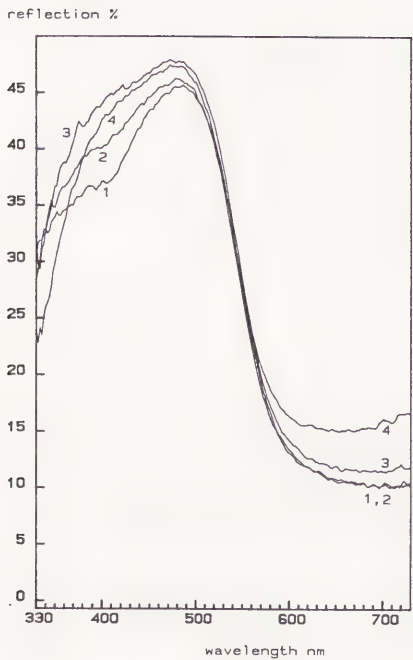
8. Change of colour (CIE ΔE 2 D65) of grey-green feather (o) with exposure to UV filtered light, reflectance curves in figure 9. The comparable curves for ΔE of blue wool standards 3 and 4 are superimposed. The behaviour of the UV exposed feather was similar. Note logarithmic scales.



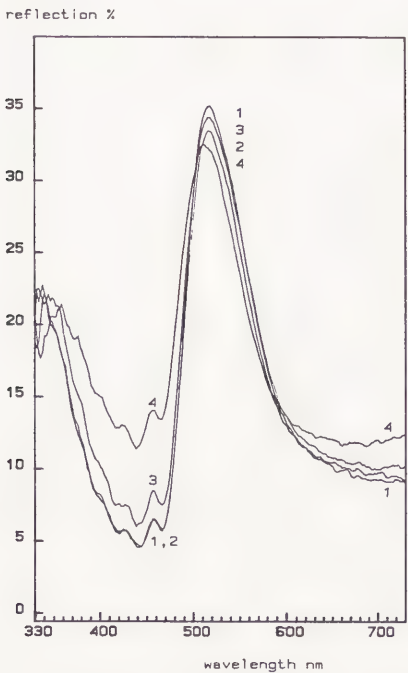
9. Change of reflectance spectra of grey-green feather after exposure to UV filtered light. The curves shown are (from bottom to top, i.e. increase in reflectance and lightness): initial values (1), after 1370 hours (2) and 13870 hours (3).



10. Change of colour (CIE ΔE 2 D65) of bright blue feather exposed to UV filtered (o) and unfiltered (Δ) radiation. In a comparison between samples with differing amounts of pigment, the absolute values of ΔE are not directly comparable. However, these two curves indicate that the behaviour of the colour in these two conditions are significantly different. Note logarithmic scales.



11. Change of reflectance spectra of bright blue feather after exposure to UV filtered light (through VA). The curves shown are: initial values (1), after 254 (2), 4780 (3), 13870 (4) hours.



12. Change of reflectance spectra of bright green feather after exposure to UV filtered light (through VA). The curves shown are: initial values (1), after 254 (2), 4780 (3), 13870 (4) hours.

EQUIPMENT AND MATERIALS

Microscal fading apparatus:
Microscal Ltd., 79 Southern
Row, London W10 5AL, UK.

Reflection spectrophotometer
ER10: Johne & Reilhofer UK,
York House, Place Farm,
Wheathampstead, Herts AL5
8SB, UK.

Acrylic sheet Perspex VA and
Standard Clear: ICI Plastics
Division, Squires Gate Works
Industrial Trading Estate,
Squires Gate Lane,
Blackpool, Lancs FY4 3RN,
UK.

Mercury discharge lamp MBTL
(discontinued and now
replaced by MLL): Philips
Lighting, PO Box 298, City
House, 420-430 London Road,
Croydon CR9 3QR, UK.

REFERENCES

1. Harmer S.F., Experiments on the fading of museum specimens, Museums Journal 22 (1922) 205-223.
2. Lord Rayleigh, The colour of the peacock's eye. Nature 121 (1928) 827.
3. Test F.H., Effects of natural abrasion and oxidation on the colour of flickers (Colaptes), Condor, 42 (1940) 76-80.
4. Ashley P.J. & Horie C.V., A list of birds with known feather colorant systems, Biological Curators Group Newsletter, 3 (1983) 331-8.
5. Thomson G., The Museum Environment, Butterworths (1978) p.23.
6. BS 1006: HTC: 1961, Humidity Test control, British Standards Institution.
7. Landmann A.W., A new apparatus for artificial daylight fading, J. British Leather Manufacturers Association, 14 (1971) 258-260.
8. BS 1006 : 1978, Colour fastness to light: Daylight, British Standards Institution.
9. ISO 105-1978, Textiles- Tests for colour fastness, International Standards Organisation.
10. Feller R. & Johnston-Feller R., Use of the International Standards Organization's Blue-Wool Standards for Exposure to Light II. Instrumental Measurement of Fading, Preprints of American Institute for Conservation Annual Meeting 1979, (1979) 30-36.
11. McLaren K., The spectral regions of daylight which cause fading, J. Society of Dyers and Colourists, 72 (1956) 86-99.
12. Billmeyer F.W. & Saltzman M., Principles of Color Technology 2nd edn., Wiley (1981).
13. McLaren K., The Colour Science of Dyes and Pigments 2nd edn., Hilger (1986)
14. Lindley F.W. & Harris P., Rate of fading of British dyed-wool light-fastness standards in daylight, J. Society of Dyers and Colourists, 78 (1962) 231-233.
15. Giles C.H., Shah C.D. & Baillie D., Economical and efficient fading lamps, J. Society of Dyers and Colourists, 85 (1979) 410-417.
16. Crews P.C., The fading rates of some natural dyes, Studies in Conservation, 32 (1987) 65-72.
17. Sander mann W. & Schlumbom F., Uber die Wirkung gefilterten ultravioletten Lichtes auf Holz - Zweite Mitteilung, Holz als Roh- und Werkstoff, 20 (1962) 287-291.

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Mrs.C.Higginbottom, The Manchester Museum, initially and later Dr.J.D.Baker, Department of Veterinary Pathology Liverpool University, kindly provided budgerigar feathers for this work. Mr.C.Hawkyard, Department of Textile Industries University of Manchester Institute of Science and Technology, donated the Microscal apparatus on permanent loan, provided access and advice on colour measuring instruments in the early stages and measured the power spectra of the radiation used for exposure. Mr.A.Brookes, Department of Physics Manchester University, enabled the design and construction of the measuring jig and the sample holders.

ABSTRACT

Recommendations for methods of assessing the condition of a fluid-preserved collection are being developed. They will include details on what collection-background information should be recorded, how to choose sample specimens that will be representative of the collection, what specimen information should be recorded, standard descriptors for containers and their contents, standard descriptors for specimen condition, methods for characterization of the preservative fluid including its identification, concentration, pH, concentration of impurities and specimen extractives and so on. It is anticipated that this will save time and improve quality in surveys of individual collections and will eventually result in a large body of internally consistent data drawn from many collections. This body of data could then be used for analyses of differences between collections and consequently between collection preservation and management procedures and for changes in preservation quality over time.

KEYWORDS

Fluid-preserved specimens,
ichthyology, herpetology,
assessment

DEFINING STANDARD PROCEDURES FOR ASSESSING THE CONDITION OF A FLUID-PRESERVED COLLECTION

SPNHC-CC Assessment Subcommittee*

Introduction

Fluid preservatives, primarily but not exclusively ethanol-, isopropanol- or formalin-based solutions are used for the preservation of specimens in most branches of biological sciences. This is especially true in the fields of ichthyology and herpetology where fluid-preserved specimens compose the great majority of collections. Although museums have been collecting these specimens for several hundred years (Whitehead, 1970) and by now hold several hundred million examples, they have rarely been subjected to systematic conservation documentation (Garrett, 1989). Thanks largely to increased funding for the conservation of natural history collections, from, for example, the Institute of Museum Services in the United States, it is expected that there will be resources available to perform conservation documentation on a number of these collections in the near future. With these facts in mind the Society for the Preservation of Natural History Collections - Conservation Committee has assigned the Assessment Subcommittee the task of recommending standard methods for assessing and reporting the condition of fluid-preserved specimen collections.

It quickly became apparent that in many areas further research or at least communication between workers in the field would be essential before specific methods could be recommended. Consequently, this paper will describe the type of information sought and aspects of the methodology being considered rather than details of methods which are yet to be decided.

The general categories of information sought include both general collection information and information about individual containers, specimens and fluids. Methodologies that must be developed include: a method for sampling collections that will allow reliable comparisons to be made between collections and through time; methods for characterizing specimen preservation quality that give at least semi-quantitative results and are both repeatable and reproducible by independent observers; and methods for analyzing fluids for both major and certain significant minor constituents.

Collection Information

Collection history

The history of the collection as a whole is a major determining factor of the current condition of the collection. Aspects of the history that will be recorded range from the geographical location of the collection at a macro level (country, state, county, city) to the specific location of the collection within the institution in which it is housed. With regard to the latter, it is necessary to consider the physical location and environment of the storage room itself as well as the type of housing for the specimens throughout the history of the collection. This information will only rarely be available as part of any collection's documentation and its procurement will rely on searches of museum archives and/or on oral histories.

In addition, it is important to document the growth of the collection over time and the periods of activity of individuals responsible for major amounts of collection and curation. This information may make it possible to associate samples with specific preparation procedures and materials.

Preparation, collection management and conservation procedures

Preparation techniques are rarely fully documented. Generally a standard protocol exists with variations carried out as the need arises. Written protocols will have to be linked to the time period of use as well as to the individuals who used them. Procedural information should include details concerning the method of specimen collection, method of killing, time from death to fixation, presence/absence of freezing before fixation, fixation techniques, and method of transfer to permanent preservative.

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The history of specimen use, both in-house and on loan, will have to be recorded. Procedures used during the use and maintenance of specimens certainly affect the condition of the specimens and these will also be recorded. These procedures range from how specimens are physically handled during identifications, cataloging, and research to protocols for maintaining fluid levels. Relevant details for the latter include how solutions are prepared, how frequently fluid levels are checked, and how fluid content is replenished.

Selection of Samples

The development of a scheme for sampling any given collection is critical to the success of this project but is proving to be one of the most difficult aspects to develop. Much of this difficulty arises from the question of whether sample selection should be completely random or whether and to what extent sampling should be directed. The sampling could be directed in many ways that are certain to or suspected to improve the utility of the data. For example, it would seem entirely reasonable to preferentially select specimens for which reliable records of preservation treatment history (*i.e.*, knowledge of field killing and fixation techniques and lab procedures for integration into the collection) are available. This would improve the utility of the data for statistical testing of the possible superiority of one treatment sequence over another in addition to reducing the need to analyze for the possible presence of exotic preservatives. Unfortunately, however, it could also introduce a bias to the data that would reduce the reliability of other comparisons between collections and within the one collection over time. Similar arguments can be made for a host of other specimen characteristics and storage parameters some of which are mentioned later.

Consequently, it is probable that a scheme for sampling that is random among specimens but ordered among collection space geometry will be adopted. The scheme for determining which specimens are selected will be designed to provide a certain minimum number of samples, perhaps fifty. This number is slightly more than sufficient to ensure that all anticipated multivariate analyses will be statistically significant. This excess is considered necessary to permit the exclusion of samples from analyses for which they are not suited. For example, the data from a sample that was stored in a formaldehyde and water solution might not be included in an analyses of the relation between alcohol concentration and dissolved calcium.

This set of fifty samples will form a core set of data that can be used for collection and time intercomparisons. In addition to this sample set, and depending on collection size and distribution, availability of resources, and the interests of the individual performing the assessment, additional samples could be taken to improve representation or render the data more useful for specific purposes.

Specimen characteristics and storage parameters that might guide further sample selection include (but are certainly not restricted to): container type and size, specimen age, quality and completeness of information on specimen history, variation in specimen to fluid volume ratio, variation in headspace to fluid volume ratio, different species or a particular common species, and ease of visibility, environmental stability or light levels in particular locations. The manner in which the extended sample set is drawn will become important information and will have to be completely and accurately recorded.

Sample Information

Sample and container identification

The unit of study for assessment of fluid-preserved specimens includes both the container and its contents at a point in time. Ideally, the goal is to trace the history of the container and its contents through time. However, in some cases these histories may differ. If the specimens are catalogued by lots, then the history of the container is probably the same as the history of the contents. Even if the specimens are catalogued individually there is a chance that specimens occupied different containers over time. The sample identification system will, therefore, be designed to make it possible to track the histories of containers and contents separately.

Container and contents descriptions

Descriptions of the container should include data such as the material and brand name of the container, the materials and sources of lids and liners, and the size of the container. These descriptions will necessitate the development of a dictionary of container types to standardize observations.

Descriptions of the contents pertain to the specimens, fluid, labels, and miscellaneous components found in the container. Assessment of specimen preservation quality is discussed separately below, but certain information dependant on the specimen will be included here. For example, the fluid to headspace ratio (with specimen immersed) and the specimen to fluid ratio will be recorded in addition to the actual amount of fluid present. Data describing the label(s) will include the purpose of the label(s), size, materials and

inks, if present, the material of anything used to attach a label to an individual specimen, and the condition of the label(s) and attachments. Examples of miscellaneous components to be considered include cheesecloth-wrapped embryos and glass vials or capsules that contain microsamples.

Identification and Analysis of Fluids

Identification

Ideally, the major constituent in the preservative fluid should be known. However, in reality, collections may contain a variety of preservative fluids and the identity of the fluid in any particular container may be unknown. Discrimination of alcoholic solutions from other types of solutions is generally possible on the basis of density measurements. Distinguishing ethanol from isopropanol solutions and identification of chemicals such as glycerol and aldehydes and cations such as arsenic and mercury will require development or adoption of specific chemical tests.

Concentration of primary constituent

Density determinations are considered the best indicator of alcohol concentration in simple alcohol-water solutions. Standard procedures for obtaining, interpreting and reporting the results of density measurements will be detailed. The question of if and how density can be used to indicate concentration in more than two component solutions will not initially be addressed but will have to be considered before an assessment of a collection containing many such samples is possible.

In cases where formaldehyde is the major constituent of the solution titration is probably the best method of quantitative analysis. Simplified procedures for performing such titrations are being investigated.

Hydrogen ion activity and titratable acidity

Hydrogen ion activity (pH) and total titratable acidity are indicators for some aspects of both past and future deterioration. Past deterioration is indicated since acidity derives primarily from generation of acidic oxidation products of the specimen, the preservative or both and future deterioration is indicated by, as one simple example, the potential for and rate of specimen decalcification. Consequently, the development or adoption of a reliable means of measuring pH in alcohol-water solutions and of performing rapid titrations with reasonable accuracy is an important part of this project.

Initial experiments have shown that colourimetric pH-measuring test papers tend to give scattered results when compared both among variations of themselves and against potentiometric measurements. In contrast, potentiometric measurements, made with a glass, pH-sensing electrode, tend to give consistent results. Equipment specifications and standard procedures for calibration and measurement will be developed to ensure that pH measurements are reliable and repeatable. When these specifications and procedures are established then they will be used to aid in finding appropriate indicators and establishing procedures for the determination of total titratable acidity.

Minor constituents

Methods of easily and reliably recording the colour of fluids and of identifying and determining, at least semi-quantitatively the concentrations of dissolved or dispersed material such as calcium, protein, lipids etc. in the fluids are also being considered. These records will provide information on the extent of specimen deterioration, albeit complicated by the fact that solutions might have been replaced without record, and they may provide information on unrecorded additives to either the original fixative or to the storage fluid.

The establishment of protocols for storage of fluid subsamples for later analysis in central laboratories is also being considered.

Specimen Preservation Quality

Specimen preservation quality is inarguably the most important parameter to be measured in an assessment of the condition of a fluid-preserved specimen collection. However, methods for measuring preservation quality of fluid-preserved specimens are not well established. In addition, efforts to locate methods of objective, non-invasive methods of preservation quality in the food technology literature have brought to light nothing that is considered useful. Consequently, we considered the possibility of constructing simple devices to provide numeric indications of specimen condition parameters such as firmness, flexibility and colour. This too had to be abandoned due to the great variety in initial specimen morphologies and textures, the uncertainty of original colouration and so on.

As a result, we shall have to adopt somewhat subjective measures of specimen preservation quality. Nevertheless, we expect that, by careful

selection of parameters, it will be possible to produce a general assessment of specimen condition. Further, by providing clear examples of degrees of deterioration against which samples can be compared, it should be possible to rank aspects of preservation quality on a five division scale with good repeatability between independent observers.

It is expected that different parameters will be useful for different phylogenetic classes to take advantage of the sensitivity of particular body parts to physical damage and to chemical or structural deterioration. Taking fish collections as an example, parameters that could be determined would include: extent of specimen completeness, extent of mechanical damage, caudal muscle tissue texture, texture of muscle tissues exposed by body cuts, adherence of scales, degree of cracking of anal fin rays, extent of loss of original colour patterns, extent of discolouration (e.g. browning), among others. Although this will mean somewhat different assessment criteria are applied to collections housing different phylogenetic classes, it is expected that general specimen conditions based on suitable combinations of parameters will still be intercomparable.

Conclusions

It is apparent that much diverse yet significant information can be obtained during an assessment of the state of a fluid preserved collection. This simple fact creates the most difficult problems to be resolved in designing the assessment procedure. These involve the trade offs between number of specimens analyzed, number of parameters measured and accuracy of each measurement. It is probable that as assessments are completed on different collections then the utility of individual parameters and of the degree of accuracy to which they are determined will become better known. Thus, assessment procedures are expected to evolve over time as more assessments are performed. It should still be possible, however, by employing standard procedures, to maintain compatibility of data both between collections and over time.

References

- Garrett, K., 1989. "Documentation guidelines for the preparation and conservation of biological specimens," Collection Forum 5(2):47-51.
- Whitehead, P.J.P., 1970. "Museums in the history of Zoology," Museums Journal 70(2):50-57.

Working Group 14

Graphic Documents

Documents graphiques



ABSTRACT

The conservation department of the National Library of Austria supported a conservation project of water damaged paper, parchment and photographic documents from the Tiroler Landesmuseum. The items were damaged as a result of a flood in 1985. The material was immediately stored deep frozen in a cold storage facility. The National Library supported the conservation of the items by freeze drying, using a freeze drying chamber which is part of its mass conservation equipment, originally developed for the treatment of embrittled newsprint. In a three year working period the 40 m³ were freeze dried with satisfactory results. The technical parameters of the drying operation are described.

KEYWORDS

ARCHIVAL MATERIALS, PAPER, PARCHMENT, PHOTOGRAPHS, WATER DAMAGE, FREEZE DRYING.

CONSERVATION OF WATER DAMAGED MUSEUM AND ARCHIVAL DOCUMENTS

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From 1987 to 1989 the conservation department of the Austrian National Library was involved in a conservation project dealing with the treatment of 40 m³ of water damaged museum and archival documents. The material to be treated was severely affected by water and covered with mud. It belongs to the collection of the Tiroler Landesmuseum Ferdinandeum in Innsbruck consisting of objects of various materials from the historical and natural science department. The damage was caused by a flood of the river Sill in August 1985. When the National Library was asked for conservation support, it could be stated that 10% of the collection was completely lost, and that 30% was damaged only to a small extent and could be treated in the conservation department of the museum in Innsbruck. The remaining part of the damaged collection, about 60%, was immediately evacuated from the flooded storage areas and transported to a cold storage facility of a food stuff company in order to prevent irreversible massive losses due to biological attack (1).

Immediately after the flood, the damaged objects were wrapped without cleaning in freezer paper and stored in boxes. Unfortunately it was not possible to catalogue the items before packing and therefore complete documentation of the objects was not possible.

The conservation treatments included freeze drying of the deep frozen material. In order to freeze dry the stocks in the most economical way possible with respect to the mass to be treated the conservation department of the Austrian National Library was asked for technical support.

This was mainly because an efficient freeze drying chamber is available at the Austrian National Library which permits the drying of approximately 0.3 m³ per drying run. The chamber, which is part of the technical equipment of the mass conservation technique developed at the National Library to deacidify and strengthen books printed on groundwood paper or bound newspapers, was installed in 1986. The freeze dryer is the backbone of this mass conservation technique, which is based on an aqueous immersion operation of book blocks after removal of the book covers. The process has been in routine operation since 1987, and is mainly applied to preserve the library's large collection of embrittled newspapers. From the very beginning of the development of the mass conservation process in Vienna it was imperative to search for a financially viable technique. One important requirement among others (3) was the flexibility of the technical installation for additional conservation purposes, which is fulfilled due to the fact that the freeze dryer can be used for drying water-damaged library and archival materials. The flexibility of the technical equipment of the "Viennese Process" is an important advantage in comparison to other mass conservation technologies as listed in Table 1.

The chamber available is a routine freeze drying chamber, USIFROID SM.H.601. It has a capacity for horizontal loading on seven shelves which are spaced at intervals of 72 mm. The total area available is about 7 m². The shelves are equipped with a heating system which can be used to supply additional heat during the drying process in order to compensate for that lost as a consequence sublimation of the water. It can also be employed to decrease the overall drying time. The drying system is equipped with a condenser with a maximum ice capacity of 100 kg inside the drying chamber.

The items to be treated included colored maps, herbal specimens, books, magazines which are partly printed on loaded paper, parchment documents, photographic prints and a number of archival materials where a large variety of writing materials for inscriptions had been used.

TECHNOLOGY	PROCESS	AGENT	USER / DEVELOPER
CHEMICAL DEACIDIFICATION CHEMICAL PAPER STRENGTHENING	AQUEOUS LIQUID PHASE IMPREGNATION FREEZE DRYING	CALCIUMHYDROXIDE + METHYLCELLULOSE	ÖSTERREICHISCHE NATIONAL-BIBLIOTHEK, WIEN REGULAR OPERATION SINCE 1987
	AQUEOUS LIQUID PHASE IMPREGNATION	MAGNESIUM - HYDROGEN CARBONATE CARBOXY METHYL CELLULOSE INK FIXATION BY CATIONIC / ANIONIC ACTIVE AGENTS	NIEDERSÄCHSISCHES STAATSARCHIV BRÜCKEBURG (FRG) IN DEVELOPMENT
	NON AQUEOUS LIQUID PHASE IMPREGNATION EXPOSURE TO γ -RAYS	METHYL METHACRYLATE ETHYLACRYLATE DIMETHYLAMINOETHYL-METHACRYLATE	BRITISH LIBRARY, LONDON IN DEVELOPMENT
CHEMICAL DEACIDIFICATION MECHANICAL PAPER STRENGTHENING	PAPER SPLITTING INTRODUCTION OF A NEW CARRIER AQUEOUS LIQUID PHASE IMPREGNATION	CALCIUMHYDROXIDE + COTTON LINTERS AS NEW CARRIER	DEUTSCHE BÜCHEREI, LEIPZIG REGULAR OPERATION SINCE 1980 MECHANIZATION IN DEVELOPMENT
MECHANICAL PAPER STRENGTHENING NO DEACIDIFICATION	VAPOR PHASE DEPOSITION OF SYNTHETIC CONSOLIDANT	PARALYNE	COMMERCIAL PILOT FACILITY FULL SCALE PLANT IN DEVELOPMENT

Table 1

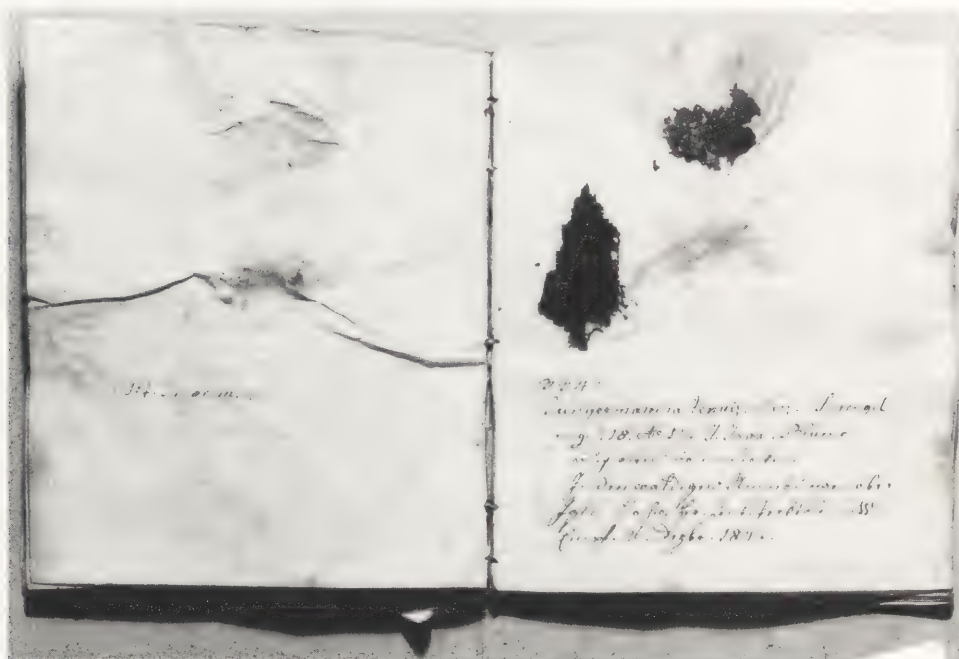
Mass deacidification & restrengthening techniques for library and archival holdings.

The frozen, water damaged, objects were sent in cooling boxes in a monthly schedule to Vienna and stored in cooling facilities at -28°C . No cleaning of the damaged material was possible before the drying process. The freeze drying chamber allows a maximum drying volume of about $0,3 - 0,4 \text{ m}^3$ within 48 hours. Freeze drying of the Innsbruck collections in 1987 and 1988 was undertaken only at the weekends in order to avoid interruption of the newspaper conservation program.

The results achieved with this treatment can be regarded as satisfactory. Before subjection to the freeze drying process, the items were separated according to their material composition. The main object of drying herbal specimens was to stabilize them in order to identify and assess their condition and value. This in turn enables the custodian to decide whether the objects have to be replaced or complete subsequent restoration will be necessary. The drying process did not affect the plant material, and the labels attached with various adhesives or by means of adhesive tapes remained in place. The writing of the labels remained legible. The herbal specimens were dried at an internal chamber pressure of 2 mb and a final shelf temperature of 40°C . All the paper objects have retained their flexibility, whereas the plant material is extremely brittle and fragmented. (Fig. 1, 2).

Figure 1

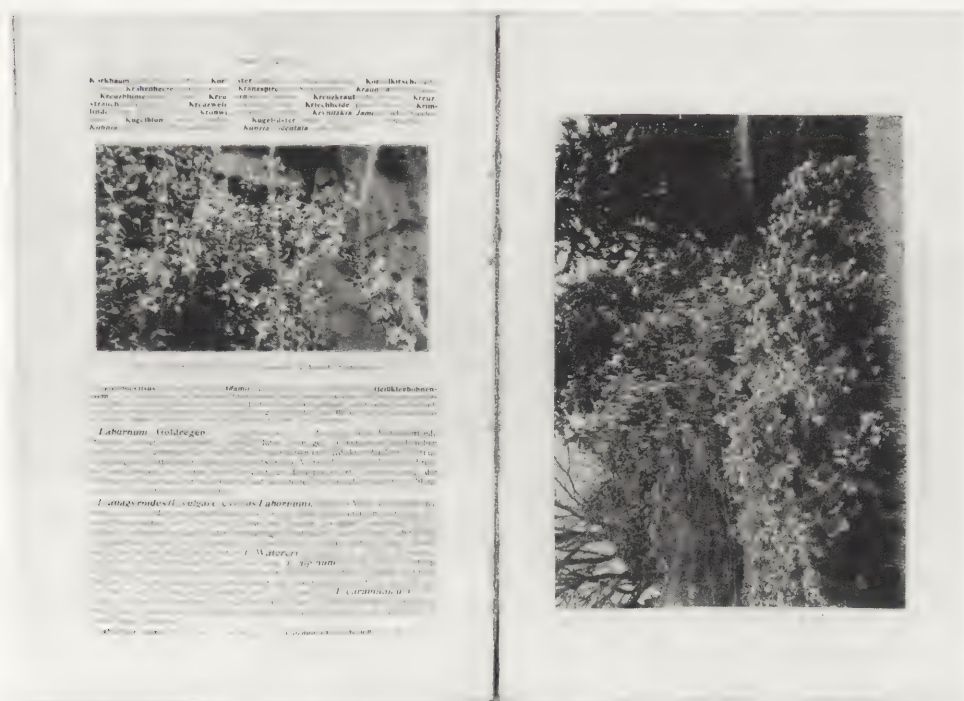
Herbarium Specimen from 1843 after drying, label written in iron gall ink.



Books and archival material were dried, using identical temperature and pressure parameters. In this way they could be transformed to a usable condition. Especially surprising was that even books printed on loaded paper with starch and casein as binding media could mostly be reopened without difficulties after treatment. Sometimes the half tone of colored prints had been partly bled out as a result of immersion in water (Fig.3).

Figure 3

Book printed on loaded paper, binding medium casein, freeze dried and reopened.



A special problem was the drying of parchment documents which had wax seals attached. It is known that parchment alters its structure after aqueous immersion. According to freeze drying tests of leather and parchment samples carried out at the Centre de Recherches de Documents Graphiques in Paris (3) it was observed that freeze drying of parchment causes problems. Due to structural changes in the material, an increase in thickness and a decrease in elasticity occurs. Furthermore, shrinkage in the dimensions of parchment items of about 4% often can be observed. According to published findings these dimensional and mechanical changes are reversible by subsequent remoistening of freeze dried parchment items in a humidity chamber and careful stretching and pressing.

Freeze drying of parchment documents was carried out at an internal chamber pressure of 2-3 mb. The shelf temperature was limited to 10 °C maximum. Control of drying time and supervision of temperature was conducted by means of thermocouples. The drying process was immediately stopped when the temperature of the parchment samples exceeded 1 °C. The result of the drying procedure was satisfactory. The parchment documents remained flexible and the wax seals unaffected (Fig.4). It could not be judged whether the dimensions of the parchment documents had changed during treatment since original dimensions of the documents had unfortunately not been recorded. Nevertheless, all freeze dried parchment documents could be regarded as usable after treatment. Subsequent cleaning and remoistening of the documents resulted in an almost complete restoration of the optical and mechanical properties of the individual items.

All water damaged material proved to be infected by molds and bacteria. Therefore, after freeze drying, sterilization of all the items was carried out with ethylene oxide in a nearby facility belonging to the Ethnographic Museum of Vienna before they were sent back to Innsbruck for subsequent cleaning and restoration.

The conservation program described proved to be an economically optimal solution in this special case. Handling, drying and subsequent disinfection in Vienna was free of charge with the exception of the investment of additional cooling facilities in the Austrian National Library, amounting to about 3.000.-\$. In addition, the museum had to pay about 850 US \$ per month to rent the space in the cold storage facility near Innsbruck and about 500 US \$ for the monthly transport of the deep frozen objects to Vienna and the return of treated items respectively.

From 1989 onwards the freeze drying chamber could be exclusively utilized for this project. This year about 25 m³ were freeze dried and disinfected. The total conservation program could thus be completed with satisfactory results in December 1989, having lasted less than three years testing and maintenance of the equipment included.

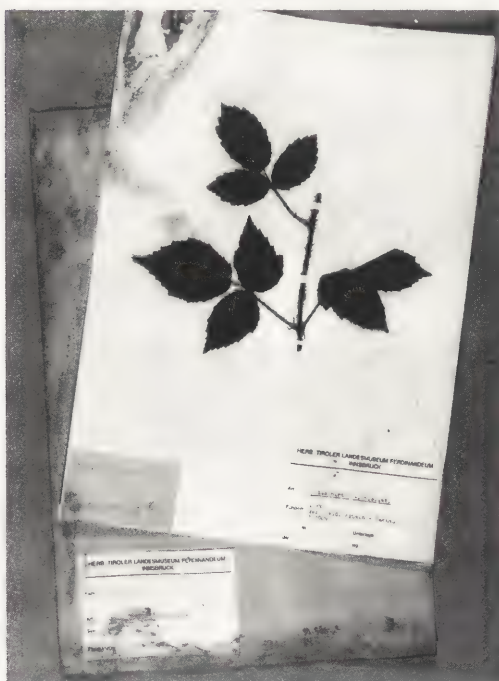


Figure 2
Herbarium Specimen from 1909, two labels printed in black ink plus typing in black ink, one written in pencil.

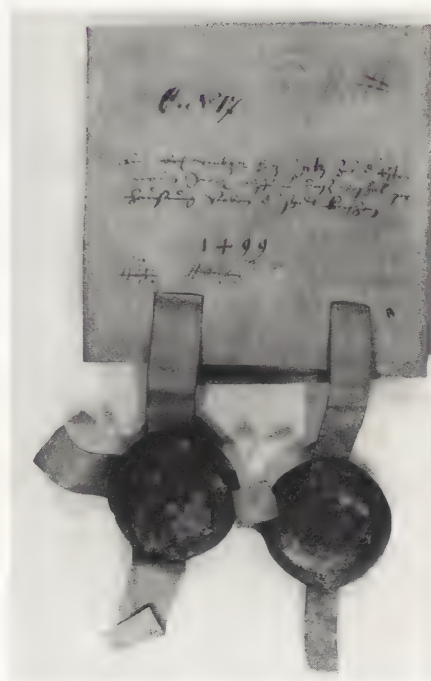


Figure 4
Parchment document from 1499 after freeze drying.

References

1. M. Klingler, "Hochwasser im Museum - Folgen und Bewältigung", Restauro 98, (1988): 95.
2. G. Banik, W.K. Sobotka, "Improvement in the Permanence of Long-Term Storage of Newsprint", in: H. Banks Ed., Advances in Printing Technology, Vol. 19, Pentech Press, London, 1988: 346.
3. F. Flieder, F. Leclerc, C. Chahine, "Effet de la lyophilisation sur le comportement mechanique et chimique du papier, du cuir et du parchemin", ICOM-Committee for Conservation, 5th Triennial Meeting, Zagreb, Preprints, 78/14/8.

ABSTRACT

This article summarizes research into the stabilization of rag paper (circa 1899) through immersion treatment with 100 mM sodium and tetraethylammonium borohydride. The effect of prior aqueous deacidification with magnesium bicarbonate upon the permanence of cellulose was also explored. Data was obtained through analysis (viscometric average degree of polymerization using the solvent cadoxen) of treated samples before and after humid accelerated thermal ageing (70°C, 50% RH for 84 days). Results demonstrated that borohydride treatments can significantly improve the long-term stability of cellulose. Data analysis revealed the importance of removing ketone and aldehyde carbonyls from oxidized cellulose prior to viscometric analysis with alkaline cellulose solvents.

KEYWORDS

borohydride; deacidification; degree of polymerization; accelerated ageing; stabilization.

THE STABILIZATION OF CELLULOSIC FIBRES BY BOROHYDRIDE DERIVATIVES

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Introduction

Historically, borohydride derivatives have been used as a chemical reducing agent in synthetic organic chemistry and as a chemical stabilizer and bleach in industrial processes. In the past number of years, they have been increasingly recognized as being useful in the conservation treatment of cellulosic paper and textiles. Research into their properties has been going on at the Library of Congress (1), University of Maryland (2,3), the National Library in Australia (4), and the Canadian Conservation Institute (CCI) (5-7).

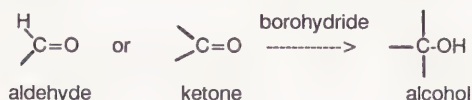
All of the chemical uses of borohydrides relate to the fact that they are reducing agents. Therefore, it was natural that their first introduction into conservation was as an anti-chlor for oxidizing bleaches. They were shown to be particularly valuable as an anti-chlor for chloramine-T (7). In fact, using borohydrides as an anti-chlor is the only way in which one can be positive that all of the chloramine-T is being removed. However, CCI's investigations into this area quickly demonstrated that they have far more value as bleaches for general cleaning and stain removal (5).

As a follow-up to their initial observations, CCI investigated the effects of solvent, reagent concentration, fibre type, and prior deacidification upon the bleaching efficiency of borohydrides (5,8,9). They have also looked at the rate of yellowing of fibres after treatment (5,6). As the final phase of the investigation of the use of borohydrides as bleaches, a series of treatments was carried out on a wide variety of artifacts. They included chalk drawings, watercolours, conte crayon, charcoal drawings, intaglio prints (with and without hand-colouring), lithographs, and pencil drawings¹. The solvent used was either ethanol or water; local, immersion or suction table methods of bleach application were used. Good results were obtained for the removal of the generalized discolourations as well as the elimination of adhesive residues and stains from pressure sensitive tapes, starch adhesives, and protein glues. The tone of the paper was well preserved in most cases, including those situations in which the paper substrate contained coloured pigments or dyes.

In addition to their use as a reducing agent bleach, borohydrides are able to stabilize chemically the cellulose in paper and textiles. For example, investigations of sodium borohydride as an anti-chlor showed that it was able to slow down the reversion process after bleaching (6). Since colour reversion is a degradative process, anything which slows it down can be considered to be a stabilization procedure.

There are two important degradation mechanisms for celluloses: the first is oxidation, and the second is acid hydrolysis. One of the most important chemical products of oxidation of the cellulose molecule is the carbonyl group. The carbonyl groups also accelerate and initiate more degradation. Therefore, it seems reasonable that if it is possible to remove the carbonyl groups through some chemical process, stabilization of the fibres would follow.

As the equation below illustrates, borohydrides specifically react with two types of carbonyls, ketones and aldehydes, and reduce them back to the original alcohol species. In effect, one is reversing oxidation.



In past projects², CCI has investigated three borohydride derivatives, i.e. the sodium, tetramethylammonium, and tetraethylammonium salts³. Their reducing action is quite similar in terms of their ability to react with carbonyls, but their working properties are quite different. A discussion of the chemical characteristics of borohydrides which are most relevant to the conservator are outlined in the conservation literature (5,7).

The largest difference in these working properties exists between the sodium and tetraethylammonium salts. This paper describes a scientific study which compares the ability of these two derivatives to stabilize cellulose through the reversal of oxidative changes. The effects of the second degradation mechanism, acid hydrolysis, was also investigated by alkalizing sample material with magnesium bicarbonate. As conservators frequently deacidify objects prior to treating them with borohydrides, this variation in the treatment plan is particularly appropriate. The long-term effects of

¹ These treatments were carried out in co-operation with the following conservators: David Tremain, CCI; Adam Karpowicz, Owens Art Gallery, Sackville, New Brunswick; Karen Graham, Canadian War Museum, Ottawa; and Janet Cowan, Royal Ontario Museum, Toronto.

² The research reported in this paper deals with the sodium and tetraethylammonium salts only.

³ Some chemical companies or technical literature may refer to the borohydride anion as "tetrahydridoborate".

the borohydride and deacidification treatments were investigated by determination of the viscometric average degree of polymerization of samples before and after accelerated ageing at 70°C and 50% relative humidity for twelve weeks. In order to provide a useful reference point, suitable control samples were included.

Experimental

The paper used in these experiments was a rag ledger paper composed of linen fibres and manufactured in 1899. Seven samples of approximately 3 g each (1 sheet) were taken from the same sewn section of the book. The samples were processed as illustrated by the flow diagram below (see Figure 1). The individual treatment sequences involved one or more of the following procedures:

1. Immersion in an aqueous solution of magnesium bicarbonate (5.7 mg MgCO_3 dissolved per ml or 1630 ppm of magnesium) for 40 min and then allowed to air dry overnight. Samples were left for at least three days before being processed further.
2. Immersion in 1.5 liters of an aqueous solution of sodium borohydride (100 mM or 3.9 g per liter) for 15 min, and then washed as described in #4 below.
3. Immersion in 1.5 liters of an aqueous solution of tetraethylammonium borohydride (100 mM or 14.6 g per liter) for 15 min, and then washed as described in #4 below.
4. Washing with flowing, filtered tap water for 90 min, and then allowed to air dry overnight.

Additional 3 g samples of the untreated control (C_1), non-deacidified wash control, C_2 D(-), and the deacidified wash control, C_2 D(+), were prepared and then analyzed for cold extracted pH according to the Tappi Standard (10).

After processing was complete, the seven (3 g) samples described in Figure 1 were cut into two equal-sized pieces (1.5 g each). The viscometric average degree of polymerization (DP) was determined for one half of each sample while the other was placed in a Tenny Benchmaster Environmental Chamber at 70°C and 50% relative humidity for 84 days. After ageing, the second half of each sample was similarly analyzed for average DP.

The average degree of polymerization was determined using a Fenske viscometer equilibrated at 30°C. The solvent cadoxen (a cadmium ethylenediamine hydroxide complex, $\text{Cd(en)}_3(\text{OH})_2$) was prepared according to the method of Donetzhuber (11). Analysis was carried out in triplicate. The average DP was calculated using the following relationship of intrinsic viscosity $[\eta]_i$ and DP (12):

$$[\eta]_i = 1.84 \times 10^{-2} (\text{DP})^{0.76}$$

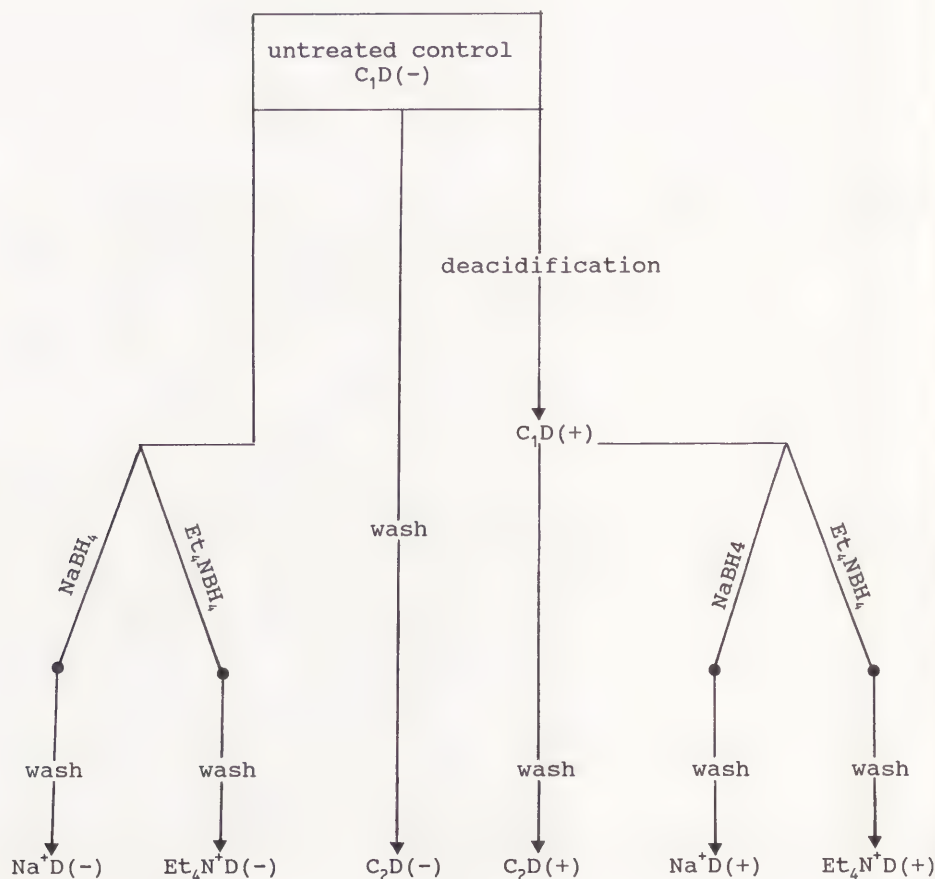


Figure 1: Flow diagram of the procedures carried out on a linen fibre paper (circa 1899) in which C_1 denotes the "no treatment" control; C_2 , the "wash control"; Na^+ , treatment with 100 mM sodium borohydride; Et_4N^+ , treatment with 100 mM tetraethylammonium borohydride; non-deacidified samples are referred to as D(-) and deacidified as D(+).

Results and Discussion

The results for the viscometric average degree of polymerization (DP) are summarized in Tables I & II. Table I gives the DP data for the unaged samples. The non-deacidified samples are designated as D(-), deacidified as D(+). The various borohydride treatments are distinguished by the chemical symbol for their salts: Na⁺ for the sodium derivative; Et₄N⁺ for the tetraethylammonium salt. As aqueous deacidification dissolves a great deal of material from paper and is, in effect, a type of washing procedure, it is not possible to have a "no treatment control" for the deacidified samples.

The first column of $[\eta]_i$ & DP data in Table I shows that the samples which had been treated with borohydride have DP's of around 380. This is true for both non-deacidified and deacidified material. The samples which had not been subjected to borohydride treatments have much lower DP values, around 300. Since it is difficult to imagine how treating fibres with borohydride can increase the DP above its true initial value, it is logical to conclude that there must be a problem with fibre shortening of samples that were not treated with borohydride. Since the D(-), no treatment control, also shows this DP loss, the fibre shortening must be happening during analysis and not during conservation treatment.

A reasonable explanation can be found if one considers the chemical structure of cellulose which has undergone oxidation. As described before, carbonyl groups are an important product of oxidation. According to the technical literature (13) these carbonyl groups create a point in the cellulose chain (at the site of a β -alkoxy carbonyl grouping) which is sensitive to alkali: chain breakage occurs and the polymer length is shortened. Since the solvent used in the viscometry experiments is the highly alkaline cadoxen, one can predict that samples containing significant concentrations of carbonyl functional groups will undergo a decrease in their observed viscometric DP values. Treating the sample with borohydride (as when a conservation stabilization treatment has been carried out), before DP analysis will result in a lowered carbonyl level and therefore, less sensitivity to alkali upon analysis.

If this theory is correct, one should be able to take the samples which had shown the artificially low DP values, treat them with borohydride and see a much higher DP on subsequent viscometric analysis. The values in the second column of $[\eta]_i$ & DP data represent unaged samples

TABLE I Average Degree of Polymerization of Unaged Samples

Sample	$[\eta]_i$	A* DP	$[\eta]_i$	B** DP
unwashed D(-)	1.4656	318 ± 2	1.6985	385 ± 3
washed D(-)	1.3886	296 ± 4	1.6914	383 ± 1
washed D(+)	1.4375	309 ± 3	1.6710	377 ± 4
Na ⁺ D(-)	1.6767	379 ± 1	-	-
Na ⁺ D(+)	1.6806	380 ± 2	-	-
Et ₄ N ⁺ D(-)	1.6917	383 ± 3	-	-
Et ₄ N ⁺ D(+)	1.6748	380 ± 2	-	-

* Analysis carried out after initial treatments.

** Samples chemically reduced by immersion in 1 liter of 100 mM tetraethylammonium borohydride for 5.5 hours and then washed in running water for 40 min. Viscometric analysis was performed within one week according to procedure previously outlined.

TABLE II Average Degree of Polymerization of Aged Samples

Sample	$[\eta]_i$	DP
unwashed D(-)	1.1842	240 ± 4
washed D(-)	1.3536	286 ± 3
washed D(+)	1.4528	314 ± 3
Na ⁺ D(-)	1.5226	334 ± 2
Na ⁺ D(+)	1.6400	368 ± 1
Et ₄ N ⁺ D(-)	1.5270	335 ± 2
Et ₄ N ⁺ D(+)	1.6504	371 ± 1

treated in this manner⁴. They show the predicted increase in degree of polymerization. It is important to note that the new values are also around 380. The numbers in this range seem to be a more accurate estimate for the average DP of the material before ageing. They also tell us that the original conservation treatment with borohydride had removed most, if not all of the reducible carbonyls present.

The accelerated ageing process can be expected to increase the carbonyl content of the fibres as it degrades and oxidizes the paper. As a consequence, it is logical to expect that any data obtained from analyses done immediately after ageing will not be representative of the true polymer length. As before, the carbonyl groups were removed before analysis, in order to avoid this problem. Therefore, the data in Table II corresponds to samples which were treated, aged, and then chemically reduced to remove carbonyl groups (as described in Table I) before viscometric analysis. As established during the analysis of the unaged samples, this will yield data which is more reliable and hence, more able to give information on how borohydride treatments are affecting the long-term stability of the cellulose fibres.

The long-term effect of the stabilization treatment is most easily seen through looking at the difference in the DP before and after ageing using only the data which has not been affected by alkaline hydrolysis (i.e. carbonyl groups have been removed before analysis). The percent loss or change in DP is illustrated by the bar graph shown below (see Figure 2). There are a number of conclusions that can be drawn from this information. The biggest drop in DP comes with the untreated control, showing that any of the treatments studied (even just washing) is better than doing no treatment at all. In order of importance, the borohydride treatment has the biggest effect on the long-term stability of cellulose. This is followed by deacidification second, and washing last.

One must be very careful in the interpretation of the results for the deacidified samples. As shown in Table III, this particular paper had a pH of 3.9 before treatment. This very low value is probably accentuating the positive effects of prior deacidification. Also, this rag paper appears to be one which can withstand deacidification well. We know that this is not true for all papers and certainly not true for all images. Therefore, caution should be exercised and all papers should not be automatically deacidified before borohydride treatment.

TABLE III Extracted pH of Control Samples

Sample	pH
untreated	3.92 ± 0.03
washed D(-)	5.81 ± 0.05
washed D(+)	8.65 ± 0.05

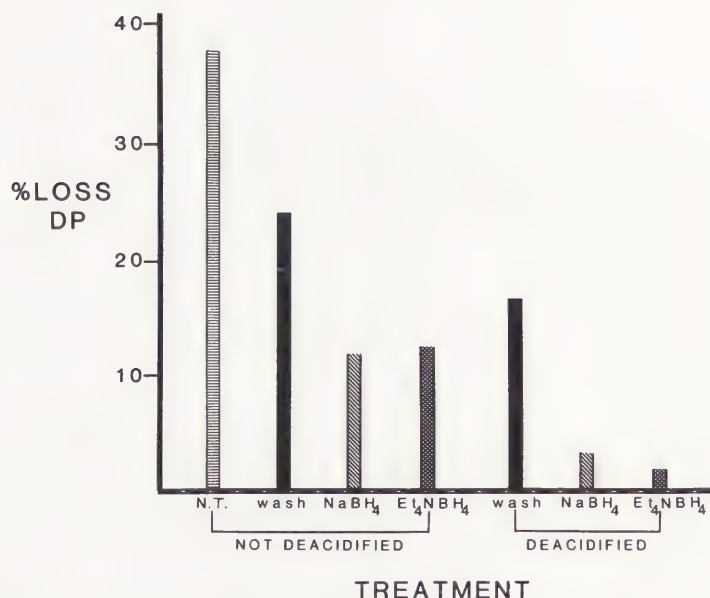


Figure 2: Percent loss in degree of polymerization (DP) as calculated from the change in DP before and after thermal accelerated ageing at 70°C and 50% RH for 84 days for samples subjected to the following treatments: no treatment (NT); wash control (wash); treatment with 100 mM sodium borohydride (Na⁺); treatment with 100 mM tetraethylammonium borohydride (Et₄N⁺); with the exception of the "no treatment" control, each treatment was carried out both without and with prior deacidification (magnesium bicarbonate containing 5.7 mg MgCO₃ dissolved per ml of solution).

⁴ In order to avoid confusion, treatment with borohydride as a stabilization procedure will be referred to as a conservation treatment; use of borohydride as part of the viscometric DP analysis will be considered to be a procedure "to remove ketone and aldehyde carbonyl groups" in order to reduce the likelihood of solvent induced degradation taking place.

However, all that aside, the results for the deacidified samples that had been treated with borohydride are truly impressive. Only a couple of percent drop in DP is observed after an entire twelve weeks of ageing. A last note on these results is that there is only very minor differences seen between the two borohydride compounds. The tetraethylammonium salt is slightly better, but the differences are small. What is probably far more important in deciding between these two is how much bleaching is appropriate for a particular artifact. One must remember that even though these chemicals are being investigated here as stabilizers, they will still have a noticeable bleaching effect. The sodium salt is a slightly more effective bleach and the conservator may want to take that into account when deciding on any treatment plan.

The data obtained in these experiments gives specific information about the use of borohydrides as chemical stabilizers. However, the analytical scientist may also find the work to be important for its conclusions regarding the effect of the alkaline solvent cadoxen on the observed DP of cellulose. This problem has been referred to in the industrial literature (14), and briefly examined by one laboratory in the conservation field (15). The fact that the experiments did not show large changes in DP⁵ due to solvent catalysed depolymerization, can be ascribed to the fact that they involved the study of new fibres which presumably have a relatively low carbonyl content. The ninety-year-old paper used in the investigation described in this article would have a much higher carbonyl content and therefore, would be considerably more vulnerable to attack by an alkaline cellulose solvent.

As concluded above, these solvent effects should not be a serious problem in investigations which involve the study of new fibres. Nor should one be concerned about the validity of conclusions which have arisen from experiments which evaluated and compared the effects of relatively degradative treatments on cellulose, e.g. bleaching with oxidizing agents. It is true that the absolute DP values are probably not accurate, but the observed relative differences between treatment sequences should be correct. It is only when one is comparing the differences among relatively non-degradative treatments performed on high carbonyl content fibres that errors in interpretation of data may result.

Conservation Applications

When designing a conservation treatment proposal that involves borohydrides, there are a large number of important factors to keep in mind. For example, in order to minimize treatment problems, the conservator must consider what concentration of chemicals to use; type of solvent; length of treatment time (i.e. compromise between effectiveness of treatment and damage to artifact); method of application (immersion, suction table, or local swab, spray, brush, etc.); what other conservation treatments need to be performed; as well as any aspects pertaining to health & safety.

It is also useful to have some knowledge of the chemistry of the borohydride derivatives being used, e.g., the chemical stability of solutions; mechanism(s) of break-down and catalysts or conditions which accelerate decomposition of solutions; decomposition products and how they could affect the artifact; as well as ways in which borohydrides could be affected by components of the artifact. Discussions of the chemistry of borohydride compounds and the carrying out of conservation treatments, are available in conservation publications (16,17).

Conclusions

Several conclusions can be drawn from the results discussed in this paper:

1. Treatment of cellulosic fibres with borohydrides significantly improves their permanence.
2. In terms of degree of stabilization, there is no significant difference between the borohydride derivatives, when used at the same molar concentration.
3. When deacidification is appropriate, i.e. the artifact is not changed or degraded, it further increases the permanence of the borohydride treated samples.
4. Through careful consideration of the chemical & physical properties of borohydrides, as well as the artifact being treated, it is possible to design a safe treatment plan for the borohydride stabilization of cellulosic fibres.

Acknowledgements

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⁵ Lee, Feller & Bogaard (15) found a 2.0 to 5.3% increase in DP following sodium borohydride treatment. The experiments discussed in this article report increases in DP of 20 to 30%, following the removal of carbonyl groups. Although the lower DP of the naturally aged fibres might accentuate differences when they are expressed as a percentage, it is still clear that very significant fibre break-down is occurring with the dissolution of aged, unreduced celluloses.

Materials

The borohydride derivatives were purchased from Alfa Products (Morton Thiokol, Inc.), 152 Andover Street, Danvers, MA 01923, USA. Sodium borohydride was listed as sodium tetrahydridoborate (cat. #87658, analytical grade) and tetraammonium borohydride as tetraethylammonium tetrahydridoborate (cat. #14123).

References

1. Tang, Lucia, "Stabilization of Paper Through Sodium Borohydride Treatment," in "Historic Textile & Paper Materials: Conservation & Characterization," H.I. Needles & H.S. Zeronian, eds., Advances in Chemistry Series #212, American Chemical Society, Washington, D.C. (1986) pp. 427-441.
2. Block, Ira, "Accelerated Ageing of Cellulosic Textiles at Different Temperatures: The Effect of Tetrahydridoborate Reduction," in "Historic Textile & Paper Materials: Conservation & Characterization," H.I. Needles & H.S. Zeronian, eds., Advances in Chemistry Series #212, American Chemical Society, Washington, D.C. (1986) pp. 411-426.
3. Block, Ira "Treatment of Cellulosic Textiles with Sodium Borohydride," Preprints of the Eighth Triennial Meeting of ICOM, Sydney, Australia (1987) pp. 345-351.
4. Lyall, Jan, "A Preliminary Study of Chemical Methods for Stabilizing Lignin in Groundwood Paper," in "Science in the Service of Conservation," N.S. Brommelle & G. Thompson, eds., Washington Congress of IIC, London (1982) pp. 79-84.
5. Burgess, H.D., "The Bleaching Efficiency and Colour Reversion of Three Borohydride Derivatives," Preprints of the Annual General Meeting of AIC, Milwaukee (1982) pp. 40-48.
6. Burgess, H.D., "The Colour Reversion of Paper After Bleaching," Preprints of the International Conference on the Conservation of Library and Archive Materials and the Graphic Arts, Institute of Paper Conservation, Cambridge, U.K. (1980) pp. 171-183.
7. Burgess, H.D., "The Elimination of Chloramine-T Residues Through the Use of Reducing Agent Anti-Chlors," Preprints of the Sixth Triennial Meeting of ICOM, Ottawa (1981).
8. Burgess, Helen D., "A Comparative Study of the Bleaching Efficiency of Conservation Bleaches, Part II: Reducing Bleaches," manuscript submitted to Journal of the AIC.
9. Burgess, H.D. and Season Tse, "A Comparative Study on the Bleaching Efficiency of Conservation Bleaches, Part III: The Effect of Prior Alkalization," manuscript submitted to J. IIC-Canadian Group.
10. "Hydrogen Ion Concentration (pH) of Paper Extracts - Cold Extraction Method: Tappi Standard T509 os-77", Technical Association of the Pulp & Paper Industry, official standard, 1977.
11. Donetzhuber, A., "Zur Herstellung des Cellulose-Lösungsmittels Cadoxen," Svensk Papperstidning, vol. 63, no. 14, (1960) pp. 447-448.
12. Zeronian, S.H., "Heat-Induced Changes in the Properties of Cotton Fibres," in "Cellulose Chemistry and Technology," Jett Arthur Jr., ed., Proceedings of the Symposium of the American Chemical Society, New York, American Chemical Society Symposium Series #48, American Chemical Society, Washington (1977) pp. 189-205.
13. Richards, G.N., "Alkaline Degradation," in "cellulose & Cellulose Derivatives," N.M. Bikales & L. Segal, eds., High Polymers: A Series of Monographs on the Chemistry, Physics, and Technology of High Polymeric Substances, Vol. V, Pt. V., Wiley-Interscience, New York (1971) pp. 1007-1014.
14. Rapson, W.H. and K.A. Hakim, "Carbonyl Groups in Cellulose and Colour Reversion," Pulp and Paper Magazine of Canada, vol. 57 (1957) pp. 151-157
15. Lee, S.L., R.L. Feller & J. Bogaard, "Relation of Cellulose Chain Scission to Hot-Alkali-Soluble Content During Thermal and Photochemical Degradation of Paper," Journal of Imaging Science, vol. 29 (1985) pp. 61-64.
16. Burgess, H.D., "Practical Considerations for Conservation Bleaching," J. IIC-Canadian Group, vol. 13 (1988) pp. 11-26.
17. Burgess, H.D., D. van der Reyden, & K. Keyes, compilers "Chapter 29: Bleaching" Paper Conservation Catalogue, N. Ash et. al. eds., Book & Paper Specialty Group, AIC (1989).

ABSTRACT.

The problem of overlapping bands in infrared analysis of paper samples has been tackled. A simple digital computation of second derivative reveals the underlying information, as shown by some examples of both authentic items and modern samples.

KEYWORDS

Paper, FTIR, band shape analysis.

NUMERICAL PROCESSING OF FOURIER TRANSFORM INFRARED SPECTRA: A POWERFUL TOOL IN PAPER ANALYSIS

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Fourier Transform Infrared Spectroscopy (FTIR) is recognized as one of the most powerful techniques in the analysis of works of art (1). Unfortunately, its application in paper analysis meets some difficulties. While heterogeneous substances such as proteinaceous glues and lignin can be easily detected (2,3), the investigation of the damage suffered by cellulose leads often to a slight modification of the spectrum (4). Furthermore, most of the information available appears restricted to a small range of frequency (i.e. 1800 to 1500 cm^{-1}) where the absorption bands of oxidized and unsaturated groups crowd together in a broad envelope. Adsorbed water introduces another problem, because its strong absorption near 1630 cm^{-1} often masks the underlying structure of other bands.

To perform the prohibitive task of obtaining some information, numerical processing of infrared data is thus inevitable. Digital computation allows the subtraction of other spectra due to heterogeneous components as well as the deconvolution of overlapping bands by analysis of band shape.

This paper deals with the second aspect, and presents a simple, unoptimized method of analysis by second derivative evaluation of absorbance spectrum.

Second derivative (DII) can be obtained by applying twice the ratio $\Delta y / \Delta x$ to the spectrum $y=y(x)$, where y stands for the absorbance and x for the frequency in cm^{-1} . By considering also the shifted data $y=y(x \pm n)$, n being the extent of shift in cm^{-1} , we obtain that DII is proportional to $y(x+n)-2y(x)+y(x-n)$. This evaluation is a simplification of the Savitzky and Golay method (5), and calculation must be done on smoothed spectra.

By application of DII to a bell-shaped infrared band, a narrow negative peak is obtained, the sharpness of which (i.e. the width at half-height) is approximately one third that of the initial band. This factor makes it possible to separate overlapping bands, although instrumental noise and bands with large standard deviation impose severe limitations. A detailed mathematical theory can be found in the literature (6) and sophisticated software based on the more complex Fourier deconvolution is available commercially.

Fig.1 shows the whole spectra between 4200 and 450 cm^{-1} (KBr technique) of the following samples:

- a) Whatman n.1 paper, taken as reference;
- b) Hypochlorite (pH7) oxidized Whatman paper;
- c) Sample b) after aging (10 days, 80°C, 76% R.H.);
- d) Authentic item from a Michelangelo cartoon.

Samples b) and c) belong to a research project presented by M.G. Plossi Zappalà in this ICOM working group, and sample d) has already been characterized elsewhere (7).

Figs.2 to 5 show the digital computation, which was performed in the most significant range between 1800 and 1450 cm^{-1} . Each figure shows both the IR absorbance (bottom) and the second derivative (top). The absorption peak at 1463 cm^{-1} was chosen rather arbitrarily as a reference for DII peak heights and resolution. If a shoulder is present (Figs. 2 to 4), its second derivative reveals an underlying peak at 1484 cm^{-1} .

Perkin-Elmer M1700 FTIR and software allowed us to perform smoothing of spectra, shifting ($n=4 \text{ cm}^{-1}$) and graphic presentation. The signs of second derivatives were reversed, a zero-line was drawn and the significant part was shaded.

The Whatman sample (Fig.2) shows a typical band near 1630 cm^{-1} due to absorbed water. Its DII is a slightly asymmetrical peak. A faint absorption in the C=O region (near 1740 cm^{-1}) is also observed.

Hypochlorite-oxidized paper shows (Fig.3) a similar IR absorption, but its DII reveals a slight 1740 cm^{-1} peak and a large band at 1636 cm^{-1} . These findings indicate the extent of oxidation: the C=O group of carboxyls and absorbed water contribute to the band centered at 1636 cm^{-1} , while the C=O ketonic group absorbs near

1740 cm^{-1} . The slight absorption in this region of an oxidized sample is not surprising, if one considers that oxidation with hypochlorite at pH 7 causes the formation of more aldehydic than ketonic groups (8) and that the former are difficult to detect by IR spectroscopy, possibly owing to hydration (4).

After aging, the hypochlorite-oxidized sample shows (Fig.4) a new strong DII peak at 1616 cm^{-1} , which could not be detected without numerical processing. Since this peak appears in a strongly discolored sample, we think that it can be attributed to conjugated groups, such as $\text{C}=\text{C}-\text{C}=\text{O}$ or α -diketones.

Fig.5 shows the complex IR structure of Michelangelo's cartoon. Its second derivative reveals the presence of ketogroups (1742 cm^{-1}) and proteinaceous glue (1542 cm^{-1} due to NH absorption and near 1670 cm^{-1} due to peptidic $\text{C}=\text{O}$ bond), while the strong DII asymmetry of the "water" band centered at 1634 cm^{-1} is due to other oxidized functions.

These few examples show the importance of numerical deconvolution of IR spectra applied to paper analysis. As far as we know, even in the main field of cellulose research the deconvolution of IR spectra dates back only to 1987 (9): as a consequence, a great deal of work ought to be done in paper conservation science to create a data-bank useful for band assignation.

This paper demonstrates that even a simple, straightforward method of digital computation greatly contributes to the knowledge of both authentic items and their modern models, chemically manipulated.

REFERENCES

1. M.J.D. Low and N.S. Baer, "Application of Infrared Transform Spectroscopy to Problems in Conservation," Studies in Conservation 22, no.3 (1977): 116-128
2. See, for instance, L. Masschelein-Kleiner, J. Heylen and F. Tricot-Marckx, "Contribution à l'Analyse des Liants, Adhésifs et Vernis Anciens," Studies in Conservation 13, no.3 (1968): 105-121
3. See, for instance, J. Marton and H.E. Sparks, "Determination of Lignin in Pulp and Paper by Infrared Multiple Internal Reflectance", TAPPI 50, no.7 (1967): 363-368
4. R.G. Zhibankov, Infrared Spectra of Cellulose and its Derivatives (New York: Consultants Bureau, 1966)
5. A. Savitzky and M.J.E. Golay, "Smoothing and Differentiation of Data by Simplified Least Squares Procedures", Anal.Chem. 36, no.8 (1964): 1627-1639
6. See, for instance, B.E. Barker and M.F. Fox, "Computer Resolution of Overlapping Electronic Absorption Bands", Chem.Soc.Rev. 9, no.2 (1980): 143-184
7. P. Calvini and G. Martinelli, "Analisi all'IR e deconvoluzione di alcune bande significative" in Michelangelo a Capodimonte, ed. Olivetti (Napoli, Museo e Gallerie Nazionali di Capodimonte: Quaderni del Restauro 6, 1988), 32-36
8. M. Lewin and J.A. Epstein, "Functional Groups and Degradation of Cotton Oxidized by Hypochlorite", J.Polym.Sci. 58 (1962): 1023-1037
9. S.N. Pandey, "Derivative Infrared Spectroscopy of Cotton Cellulose", J.Appl.Polym.Sci. 34 (1987): 1199-1208

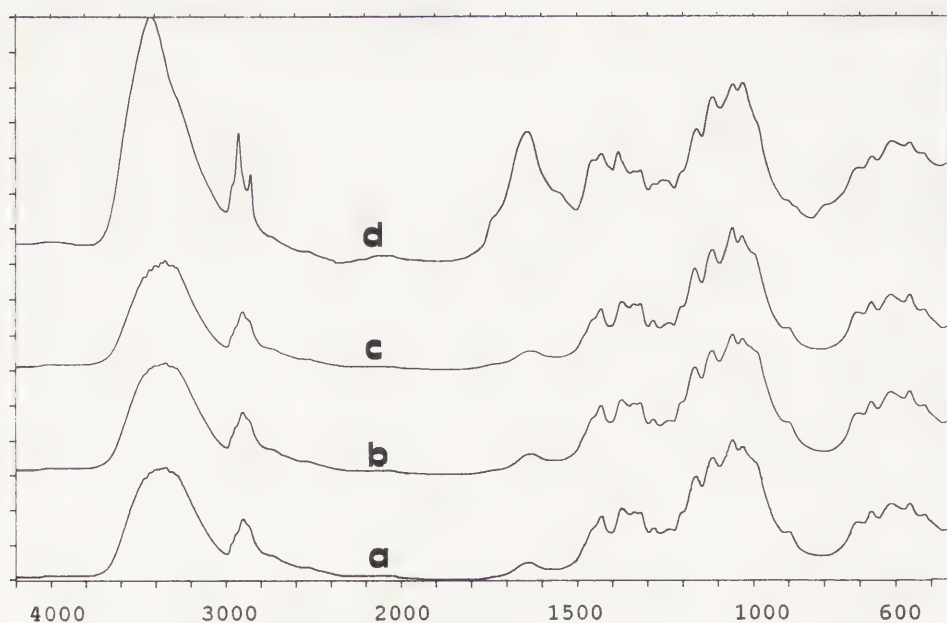


Fig.1. Infrared spectra (absorbance vs. wavenumbers) of:

- a) Whatman no. 1 paper
- b) Hypochlorite-oxidized Whatman paper
- c) Sample b), aged
- d) Michelangelo's cartoon

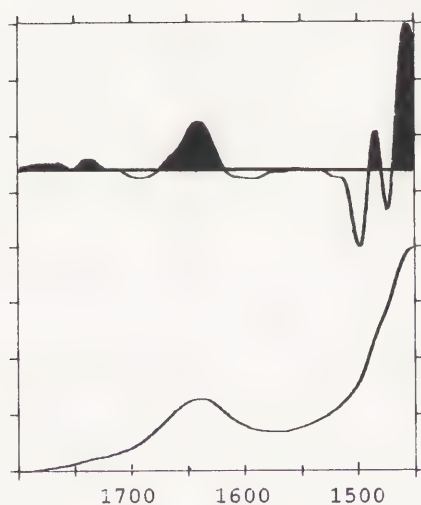


Fig.2. Infrared absorbance and its second derivative of Whatman paper

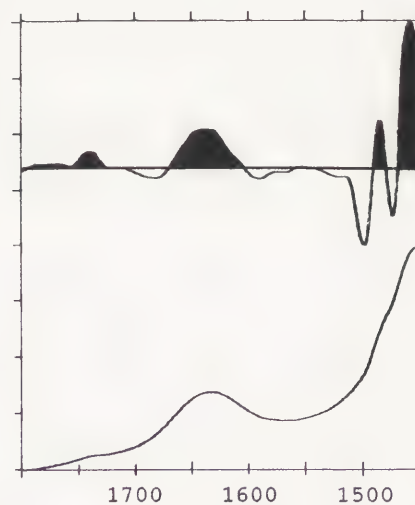


Fig.3. Infrared absorbance and its second derivative of hypochlorite-oxidized Whatman paper

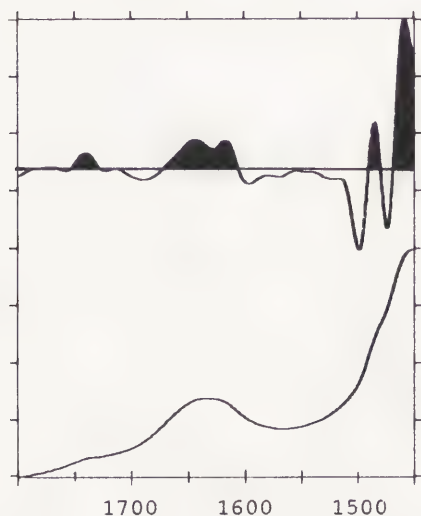


Fig.4. Infrared absorbance and its second derivative of hypochlorite-oxidized and aged Whatman paper

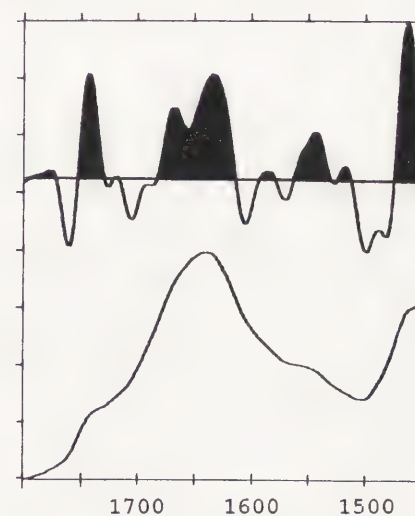


Fig.5. Infrared absorbance and its second derivative of a sample from Michelangelo's cartoon.

ABSTRACT

Research on the effect of stabilizing paper with fibrous ionite - phosphate of cellulose - was done. The purpose of this stabilization is to inactivate iron ions - the catalysts of the oxidative degradation of paper - by sorption with fibrous ionite from the production water before the casting of paper. A phosphate cellulose sorbent is recommended when filling the missing parts of documents with paper pulp in a leaf-casting machine.

KEYWORDS

Document restoration, fibrous sorbent, leaf-casting system, paper stabilization, phosphate of cellulose

INCREASING THE DURABILITY OF PAPER WHEN RESTORING DOCUMENTS BY PAPER PULP FILLING PROCESS

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USSR

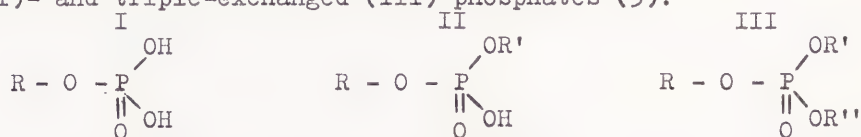
Paper, after storage for long periods, is destroyed by a hydrolysis catalyzed by acids. Various methods of neutralizing acidity can be employed. Along with the catalyzed acidic hydrolysis, however, other oxidization processes are catalyzed by iron and copper ions (Fe^{3+} , Cu^{2+}). During the restoration process, when filling the missing parts of documents in a leaf-casting machine, the effect of oxidization processes on the degradation of paper is manifested quite considerably. This is true even when the casting is done with paper pulp made of durable cotton cellulose as a base.

Various investigations have shown and proven that the presence of scant traces of such heavy metals as Fe^{3+} and Cu^{2+} accelerate the oxidative degradation of paper in the presence of moisture, and naturally reduce its durability in the course of storage (1, 4).

All the existing methods of stabilizing paper have one feature in common: direct contact of ready paper or paper pulp (if casting is meant) with a chemical agent slowing down the degradation of pulp and paper.

During its operation the leaf-casting machine uses a great deal of water, which, as is known, is the principal source of iron and copper ions in paper. The analysis of water used in the leaf-casting machine has shown that the concentration of iron ions is 0.3-0.5 mg/l, and at certain stages of the technological cycle up to 1.0 mg/l.

A study was made of a method which enhances the stability of paper in storage by means of inactivating metal ions (catalysts of the oxidative degradation) before they get into the paper, with the fibrous sorbent serving as the inactivating agent. Phosphate of cellulose, which is manufactured in a sodium hydrogen form as gauze, was used in the experiment for this purpose. In the sorbent composition there are mono (I)-, double (II)- and triple-exchanged (III) phosphates (3):



The role of the ion-exchanger is played by the mono-exchanged and, partially, double-exchanged phosphates. The exchange capacity of the sorbent is 2.5 mg-equ/g. In order to compare its efficiency the sorbent was used also in a sodium and hydrogen form.

At the first stage of the research the sorbent in a sodium hydrogen form, 100 g in mass, was placed in a specially designed filter and tested for absorption capacity in time with regard to iron ions. During the testing the production water passed through the filter with the sorbent with the speed of 0.5 l/min. Every 3-5 h the water was analyzed for iron content in it. The graphic formula of the test results is shown in Fig 1.

The experiment was conducted for 130 h. The concentration of iron in the water processed with phosphate of cellulose constituted 0.03-0.06 mg/l. The mean value of the water purification degree was at the 82 per cent level and did not go down during the course of the testing.

Then samples of paper of three compositions were cast in the laboratory leaf-casting apparatus: (1) cotton cellulose, (2) sulphite cellulose, (3) cotton cellulose with added calcium carbonate and polyvinylalcohol fibres. In so doing, part of samples were made without the use of the sorbent. In order to make another part, water was processed in advance with the sorbent in different forms. Noteworthy is the fact that iron turned out to be 0.00017 per cent, which is approximately 50 times less than in the paper made of this cellulose without the

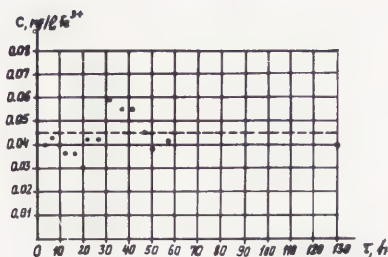
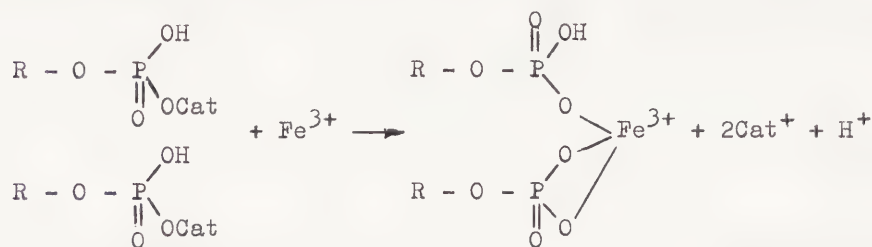


Fig. 1. The content of iron ions (Fe^{3+}) in the water depending upon the time of the sorbent operation

use of the sorbent (0.00810 per cent). It appears that during the casting, iron ions are absorbed by the cellulose from the water and accumulate in the paper. The iron content in the samples turned out to be minimal (0.00310 per cent), when before the casting the production water was processed with the phosphate cellulose sorbent in a sodium hydrogen form. The diagram of the reaction of the sorbent with iron ions can be shown in the following way:



where R is the residue of the cellulose, Cat is cation, e.g. Na^+ .

All the samples produced were subjected to a moist artificial heat ageing in a thermostat with circulating air, at the temperature of $102 \pm 2^\circ\text{C}$ for 72, 144, 216 and 288 h. Values of the flexing resistance, brightness and the pH of water extracts are shown in Fig. 2, 3.

Processing the production water with the phosphate cellulose sorbent considerably enhances the stability of paper in storage according to all indices. It is noteworthy that the processing of the water with the sorbent in a sodium form is more favourable to paper made of cotton cellulose than the processing with the sorbent in a hydrogen form (Fig. 2, curves 2 and 3). Ion exchange occurring between the sorbent and heavy metal ions contained in the water (in particular, iron ions), is accompanied in the first case by their removal from the water and the enrichment of the water with sodium ions, which results in the alkalization of the latter, which has a favourable effect on the stability of paper in storage. In the second case, the concentration of hydrogen ions, owing to the ion exchange, grows in the water resulting in its enhanced acidity. This ultimately intensifies the hydrolytic degradation of the paper. This trend is particularly vividly manifested for paper made of sulphite cellulose (Fig. 3, curves 2 and 3).

When analyzing the results, it is necessary to take into consideration that the composition of paper, made normally by means of a mechanized method of restoration in the leaf-casting machine (cotton cellulose with calcium carbonate and polyvinyl-alcohol fibres added), enhances the strength of the paper 4.2 times, and after heat ageing the strength reserves remain larger than those of polymerless paper. This is fully confirmed by the positions of curves 1 and 4 in Fig. 2.

The determination of the pH value of a water extract from each sample produced yields no new information. The value of this index for paper made of cotton cellulose in the course of artificial ageing remains at a moderately alkaline level (7.00-8.00) in those cases when calcium carbonate has been introduced into the composition of the paper, and at a level slightly lower than neutral (6.25-6.40) when calcium carbonate is not present in the composition.

Thus, the processing of water with the phosphate cellulose sorbent in a hydrogen form cannot yield the desired result, whereas the use of the sorbent in a sodium hydrogen or sodium form contributes to a considerable enhancement of the stability of paper in storage, and may be recommended for the restoration of documents on a paper base by the method of filling the missing parts with paper pulp in a leaf-casting machine.

The calculation of a probable time of the use of the filter with a sorbent under the closed cycle conditions of the operation of the leaf-casting machine has shown that 100 g of the sorbent can remain "workable" for three months. The great advantages of the sorbent are its compactness and technologically simple regeneration.

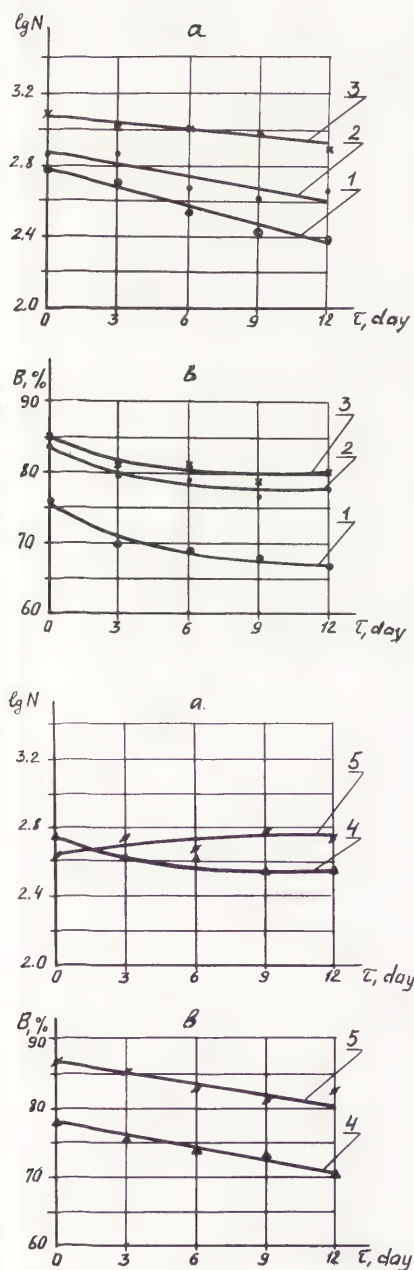


Fig. 2. Changing properties of paper made of cotton cellulose in the process of artificial ageing:
a. folding endurance (lg N);
b. brightness (B).

1, 4* - casting without processing of water by sorbent;
2 - sorbent in H^+ -form;
3 - sorbent in Na^+ -form;
5 - sorbent in $\text{Na}^+ - \text{H}^+$ -form.

*The paper contains 100% of cotton cellulose, 5% PVA fibres and 5% CaCO_3 to fibre mass.

References

1. Blank M.G., Dobrusina S.A., Temkina V.J. Stabilizatsija bumagi kompleksnymi sojedinenijami. Soobshch. I // Teorija i praktika sokhraneniya knig v biblioteke / M.E.Saltykov-Shchedrin State Public Library. Leningrad, 1983. Vyp. II. S. 47-61.
2. Blank M.G., Flyate D.M. Bumaga dlya restavratsionnykh rabot // Dolgovechnost dokumenta. Leningrad, 1981, s. 85-91.
3. Yermolenko I.N., Buglov E.D., Lyubliner I.P., Dovgalev S.I. Novyje voloknistyje sorbenty meditsinskogo naznacheniya. Minsk: Nauka i tekhnika, 1978. 215 s.
4. Williams J.C., Fowler C.S., Lyon M.S., Merrill T.L. Metallic catalysts in the oxidative degradation of paper // Preservation of paper and textiles of historic and artistic value / Ed. J.C.Williams. Washington, 1977. P. 37-61.

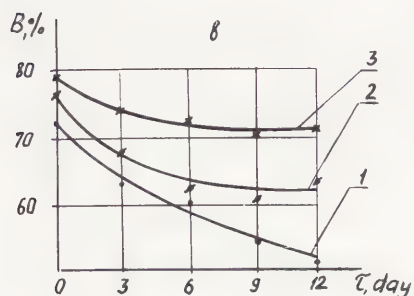
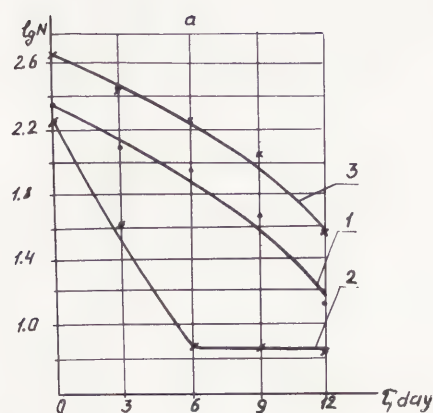


Fig. 3. Changing properties of paper made of sulphite cellulose in the process of artificial ageing. The designations as on the Fig. 2.

ABSTRACT

La restauration et le montage d'un dessin de grand format sont présentés. L'accent est mis plus particulièrement sur le montage pour lequel le restaurateur a utilisé la technique orientale du claustra habillé, sur ses 2 faces, de couches superposées à contresens de feuilles de papier japonais fin. L'intérêt de cette structure sur laquelle l'oeuvre est collée en plein, réside dans les fonctions isotropes et auto-régulatrices qu'elle confère à l'oeuvre vis à vis de l'environnement climatique externe.

MOTS CLES

DESSIN - GRAND FORMAT - MONTAGE -
TECHNIQUE ORIENTALE - CLAUSTRAS -
ANISOTROPIE - ISOTROPIE -

A PROPOS DU MONTAGE APRES RESTAURATION D'UN DESSIN DE GRAND FORMAT :
LE PONCIF ET L'ETUDE DU PERSONNAGE DE NAPOLEON POUR LE TABLEAU DU
SACRE PAR J.L. DAVID.

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I - INTRODUCTION

C'est dans le cadre de l'exposition consacrée au peintre J.L. DAVID, qui s'est tenue au Musée du Louvre au cours du 3ème trimestre 1989, qu'a été décidée la restauration du poncif du personnage de Napoléon pour le tableau du sacre. Ce dessin, appartenant au Musée de LILLE, fait partie de la prestigieuse donation de 3.600 dessins faite par J.B. WICAR à ce Musée en 1834.

Sa restauration et son montage ont été confiés au service de restauration de l'Inspection Générale des Musées classés et contrôlés à Versailles.

Si la restauration de ce dessin posait, par ses dimensions et son état de dégradation, des problèmes qui seront évoqués dans les lignes qui suivent, l'objet de cette présentation est plus particulièrement de s'attacher à décrire le procédé de montage qui a été choisi, à justifier ce choix et à en tirer les conclusions qui s'imposent pour les recherches à venir dans le domaine des supports adaptés au montage des dessins de grandes dimensions. Si, en effet, et malgré un facteur espace/temps qui amplifie les problèmes, les traitements de restauration qui leur sont appliqués sont souvent les mêmes que ceux utilisés pour les dessins de petites dimensions, le problème du montage, quant à lui, reste une question ouverte qui jusqu'à présent ne trouve que des réponses subjectives au gré des intuitions et des pratiques individuelles.

II - LE DESSIN ET SA RESTAURATION

II 1 - ETAT DE DEGRADATION

Il s'agit d'un dessin préparatoire de 1,22 X 2,00 m. Si la sanguine s'impose immédiatement comme technique graphique, l'analyse visuelle plus poussée laisse à penser qu'il s'agit plutôt d'un dessin au fusain gras ou au crayon Conté (Brevetage Conté 1795) se trouvant sous-jacent à la sanguine qui, elle, aurait pu être utilisée ici pour sa pulvérulence afin de permettre, à travers les trous ménagés le long des traits, le report du dessin.

Le trait de sanguine est noyé dans le jaunissement provoqué par l'état d'extrême oxydation du support. Il est effacé à certains endroits et, dans sa lisibilité actuelle, il est inséparable de l'effet de relief provoqué par les piquages de report.

Le support, constitué de 8 feuillets de papier vergé collés les uns aux autres par superposition, est séparé en deux par une déchirure traversant la totalité du dessin de gauche à droite au niveau de la taille du personnage.

Enfin, le côté gauche du dessin, situé sous le bras tendu de Napoléon, présente, sur 1,60 m de haut et 0,40 m de large environ, un "manque" dans lequel devait s'encasturer l'étude de Joséphine agenouillée. L'ensemble du dessin a été doublé, sans doute au début de ce siècle, d'un papier assez épais (80 g environ), velin constitué de pâte mécanique de bois de pH 4.7. De nombreuses pertes d'adhérence, observables entre le support et ce doublage, ont évolué en trous, déchirures et plis.

Le support, qui présente une valeur de pH semblable à celle du matériau de doublage, est fin (40 g environ), fragile, usé, cassant, très empoussiéré. On observe sur sa surface de nombreux plis provoqués, d'une part, par le "raboutage" des différents feuillets et, d'autre part, par un doublage maladroit. Des déchirures importantes dans le support et son doublage, induites au niveau du tracé du dessin par les piquages de report, se sont souvent prolongées au-delà de ces traits.

II 2 - RESTAURATION

La valeur du pH, extrêmement basse, du papier de doublage, imposait d'emblée une dépose de celui-ci. La fragilité du support et du tracé, nous ont amenés à préférer, après fixation du recto à l'aide de gélatine à 1 %, un dégagement à sec par lamination lente du doublage jusqu'à l'obtention d'une pellicule résiduelle fine, dégagée enfin à l'aide d'un apport contrôlé d'humidité. On a ensuite procédé au nettoyage des résidus de colle sur le verso, suivi de la remise en place et de la consolidation des déchirures. Un papier vergé 100 % coton, fabriqué par le Moulin de Larroque et possédant une texture assez proche de l'original, a été utilisé sous forme de pâte à papier pour les petites réintégrations, et sous forme de feuille pour combler la partie manquante à laquelle il a été fait référence plus haut. Dans ce dernier cas, les feuilles, pour être en harmonie avec la couleur de l'oeuvre, ont été teintées en milieu acide, par bain, à l'aide d'aquarelle Winsor & Newton. Ce traitement a été suivi, après séchage, par une désacidification.

Les feuilles ainsi teintées ont été "raboutées" pour remplacer la partie manquante. Cette reconstitution, ainsi que l'oeuvre, ont été doublées séparément une première fois à l'aide du même papier (Minogami fin 100 % Murier) et de colle d'amidon. Enfin, l'oeuvre et sa partie reconstituée, une fois rassemblées, ont été doublées une deuxième fois en utilisant du papier RK 17 (Atlantis 100 % Murier en rouleau) et la même colle que pour le premier doublage.

III - LE MONTAGE

III 1 - ETAT DE LA QUESTION ET CRITERES DE CHOIX

Les restaurateurs de dessin disposent aujourd'hui de nombreux panneaux, nid d'abeille aluminium ou carton ou encore panneaux de polystyrène ou de polycarbonate, qui peuvent, en certains cas, les aider.

Si ces matériaux, quand ils sont disponibles sur le marché, s'avèrent satisfaisants en ce qu'ils protègent les dessins des agressions physiques externes de façon plus efficace qu'un simple châssis, ils sont parfois lourds, souvent difficiles à mettre en oeuvre. Leur utilisation n'autorise par ailleurs aucune mise en tension, aussi légère soit-elle, du support papier.

D'autre part, une fixation du dessin limitée uniquement à ses bords, contrairement à une fixation répartie également sur toute la surface, induit des tensions fortes localisées dans la partie supérieure de l'oeuvre et provoque par contre-coup, dans la partie inférieure, des déformations pouvant aboutir à une dégradation.

Dans le cas qui nous intéresse ici, la fragilité du dessin de J.L. DAVID et la volonté de sauvegarder un effet de relief provoqué au niveau du trait par le piquage de report nous ont amenés à nous orienter vers un support qui, en respectant le principe de réversibilité, assurerait une répartition des forces de tension sur toute la surface de l'oeuvre, sans lui retirer la possibilité de répondre aux sollicitations extérieures provoquées par des variations de l'environnement climatique.

Le claustra de bois, préparé sur ses deux faces de couches de papier fin, superposées et alternativement collées en plein et libres, tel qu'il est utilisé en Orient, tant pour les paravents que pour les panneaux de séchage, nous a semblé répondre à ces exigences.

III 2 - ESSAIS SUR MAQUETTE DU MONTAGE CHOISI ET REALISATION

Afin de tester la faisabilité d'un tel projet, nous avons fabriqué une maquette au 1/3 de la grandeur réelle du dessin. Le claustra, en cèdre rouge (cedrela odorata, bois de faible densité, antimite), a été habillé sur ses deux faces de 6 couches superposées de papier japonais (21 g RK 17 Nao 100 % Murier) à l'aide de colle d'amidon. Pour chaque couche, les pontuseaux sont placés perpendiculairement à la couche précédente.

A l'exception des autres couches collées en plein sur les précédentes, la troisième couche et la cinquième couche, elle-même composée de 2 sous-couches, sont flottantes*.

Sur le support ainsi composé, on a collé en plein, sur une seule des deux faces, un papier vergé du XVIII^e siècle, préalablement doublé afin de simuler le montage de l'oeuvre future.

Cet essai nous a permis de comparer le comportement des variations dimensionnelles de l'oeuvre doublée par rapport au support de montage constitué comme ci-dessus. Le maintien des qualités de souplesse du papier du XVIII^e siècle, utilisé pour la simulation, ainsi que l'absence de tensions excessives ou de déformations, nous ont conduit à utiliser cette méthode de montage pour le dessin de DAVID. Nous résumons, par le schéma ci-dessous, les principes importants de ce type de montage, tel qu'il a été utilisé.

SCHEMA DU MONTAGE SUR CLAUSTRA BOIS PREPARE DE COUCHES DE PAPIER POUR LE DESSIN DE DAVID: NAPOLEON

	Denomination de la couche	Sens des Pontuseaux	Caractéristique du collage des feuilles		
	1 ^{ère} couche	H	Collées en plein sur les montants		Claustra
	2 ^{ème} couche	V	Collées en plein sur la 1 ^{ère} couche		Colle
	3 ^{ème} couche	H	Flottante. Bandes collées uniquement par leur extrémités et se superposant		1 ^{ère} couche
	4 ^{ème} couche	V	Collées en plein sur la 3 ^{ème} couche		2 ^{ème} couche
	5 ^{ème} couche	A	Constituées de petites unités collées sur les bords		Vide d'air
	6 ^{ème} couche	H	Collées en plein sur A et B		3 ^{ème} couche
	2 ^{ème} doublage	V	Collées en plein		Colle
	1 ^{er} doublage	H	Collées en plein		4 ^{ème} couche
	OEUVRE	H			Vide d'air
					5 ^{ème} couche
					Colle
					6 ^{ème} couche
					Colle
					2 ^{ème} doublage
					Colle
					1 ^{er} doublage
					Colle
					OEUVRE

LEGENDE: CLAUSTRA --- COLLE — PAPIER V: pontuseaux horizontaux H: pontuseaux verticaux

On remarque que le dessin, une fois collé sur ce support, fait totalement corps avec celui-ci. La superposition des couches, posées perpendiculairement les unes aux autres, joue dans le sens d'une certaine neutralisation des forces de tension, tendant à faire d'un matériau anisotrope un matériau isotrope.

L'ensemble dessin-montage joue par ailleurs un rôle d'auto-régulation, lors de changements subits dans l'équilibre climatique extérieur. L'accès au dos de l'oeuvre, se faisant au niveau de la 5^{ème} couche, facilite une réversibilité éventuelle.

* par opposition à "collé en plein", signifie que les couches auxquelles il est fait référence sont constituées de petites feuilles (25 x 25 cm) fixées uniquement par leurs bords. On a donc une succession de petites poches d'air d'où le terme "flottante". Ces poches ont un rôle régulateur sur le comportement du support vis à vis des sollicitations extérieures.

CONCLUSION

Ce système semble répondre, par bien des aspects, aux critères que nous recherchons pour la mise au point d'un support de montage dans la restauration des dessins de grand format. Notre souci est toutefois de nous orienter, à partir de l'expérience présente, vers la mise au point d'un support qui, tout en respectant certains des principes de base exposés ici, serait simplifié. Le principe de démultiplication des forces de tension ainsi que l'aspect auto-régulateur doivent être conservés. On peut, d'autre part, envisager d'influer sur les propriétés d'anisotropie ou d'isotropie du support de montage en jouant sur la superposition des couches et sur les propriétés des papiers utilisés au gré de la spécificité des supports d'oeuvre à traiter lorsque, par exemple, nous travaillerons sur des papiers du XXème plus anisotropes que des papiers vergés anciens.

BIBLIOGRAPHIE

- MASAKO KOYANO : Japanese scroll paintings, a handbook of mounting techniques.
Foundation of the American
Institute for conservation.
John Winter editor, 1979.
- P. WEBBER & M. HUXTABLE : Karibari, the japanese drying board. The paper conservator, Journal of the institute of paper conservation VOL.9 1985 pp54-60 P. WILLS & N. PICKWOAD editors.
- F. HERRENSCHMIDT &
C. LARROQUE : A propos d'un carton du Musée du Louvre une approche de la conservation des dessins de grand format ; pp 229-239 ; preprint des journées sur la conservation, restauration des biens culturels.
Traitement des supports travaux interdisciplinaires.
Paris, 2, 3, 4 Novembre 1989 ARAAFU.

ABSTRACT

The purpose of this project was to find new methods to relax and flatten tracing paper supports for works of art. GORE-TEX barrier was used to achieve an even and gentle relaxation without any risk for water-sensitive colours. Flattening was carried out on the suction table. This procedure allows severe undulations from tracing papers to be removed with minimal stress. Even highly water-sensitive colours are not endangered nor are the dimensions of the tracing papers enlarged.

KEYWORDS

TRACING PAPERS; WATER-SENSITIVE COLOURS; HUMIDIFICATION; FLATTENING; GORE-TEX.

CONSERVATION OF TRACING PAPERS

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1. Introduction

Works of art on tracing papers represent a severe problem in collections all over the world. Sensitivity to water, poor mechanical stability and oversized dimensions present all kinds of difficulties to conservators^{1/2}. The aim of this project was to find new gentle methods to relax and flatten tracing papers.

2. History

The Theatre Collection of the Austrian National Library owns a large number of costume and stage designs by Oskar Strnad. The architect, stage designer and artist craftsman Oskar Strnad lived from 1879 to 1935. He created décors for theatres in Vienna, Salzburg, Berlin and many other cities. From 1924 onward he worked in close cooperation with Max Reinhardt.

3. Condition

Oskar Strnad used gouache and water-colours, inks, silver and gold colours on tracing papers of different thickness for his decorative designs. The sizes vary from 250x350 mm to 700x500 mm. All papers are disfigured by a large amount of surface dirt, and some of them have tears which were mended with a precoated tape. Due to the use of water-colours the papers show severe undulations and creases.

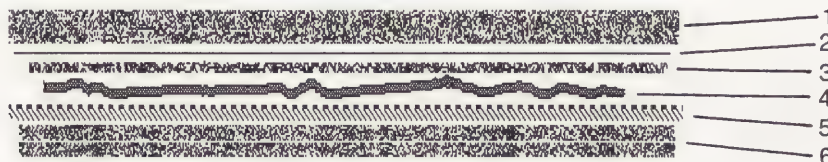
4. Treatment

After several tests GORE-TEX (R) tissue was selected to achieve an even, gentle and controlled humidification without any risk to the highly water-sensitive colours. The slow and gentle relaxation resulted in a minimal extension of the tracing papers. All other kinds of humidification enlarged them to a much greater extent. This is especially unacceptable for the conservation of architectural designs which should stay in scale.

GORE-TEX (R) barriers consist of a polyester felt on which a thin GORE-TEX (R) membrane is applied on one side. This membrane is made of especially manufactured polytetrafluoroethylene, which is hydrophobic, chemically inert and air permeable. These characteristics enable GORE-TEX (R) barriers to stop water from penetrating but allow gases, such as water vapors, to pass³. The application of GORE-TEX (R) in paper conservation was already recommended at the IADA conference in Berlin 1988. The technique presented in this paper is a slight modification of the one presented by Keiko Keyes at the Symposium 88 in Ottawa⁴. The following sandwich was used:

Figure 1

Schematic cross-section through the GORE-TEX (R) sandwich.



- 1: Felt, to apply a little weight to ensure good contact of the original with the GORE-TEX (R) membrane. The tracing paper would otherwise curl up, due to different stress in the paper during the humidification.
- 2: Melliphan (R) (optional).
- 3: Viledon (R), non-woven fabric.
- 4: Tracing paper, face up.
- 5: GORE-TEX (R) barrier, the glossy side up (membrane).
- 6: Wet blotting paper.

* Author to whom correspondence should be addressed.

This method has the advantage that the humidity penetrates very slowly and controlled into the original and only in the form of water vapor. Even an exposure of 72 hours did no harm to the water-sensitive colours used by Oskar Strnad. Thick tracing papers make it necessary to put a Melliphan (R) sheet on top of the Viledon (R) fabric to stop evaporation of the moisture before the paper is fully relaxed. If long-term exposure was needed, ethanol was added to the water wetting the blotter in order to reduce the risk of mould growth⁵. Proportion water/ethanol: 3/1 (V/V).

Surface dirt on the tracing papers was removed by dry cleaning. All kinds of old adhesive tapes had to be removed since they would have caused problems on the suction table. The objects were left in the GORE-TEX (R) sandwich until they were totally relaxed. The length of humidification treatment depends on the quality of tracing papers and can only be determined by experience. The fully relaxed drawings were then placed on the suction table, which was switched on at a low pressure beforehand. Starting on one side, the object was laid down gradually similar to the lining procedure. Remaining creases were removed by hand through gentle stretching of the paper while the pressure of the suction table was slowly increased. Fortunately most creases were located around and not in the painted areas. Therefore the stretching procedure is safe for the sensitive colours. As soon as the tracing paper lay flat on the suction table, it was covered for a short time by a Melliphan (R) sheet to increase the pressure. During this procedure the margins of the tracing papers were covered approximately 1-2 mm with Melliphan (R) strips to prevent them from lifting during drying. The Melliphan (R) sheet, covering the whole, was replaced with several sheets of blotting paper and the design was left on the suction table until it was dry. The treatment of larger objects requires the use of a humidification dome and an ultrasonic humidifier attached to the suction table. It is advisable to dry the relaxed tracing papers completely on the suction table to avoid undulations and to retain the papers' original size. The exact measurement of the length and the width of the drawings, before, during and after the treatment showed a minimal increase as illustrated in Fig. 7. The flattened papers should be stored at least a few days under light pressure. If necessary, adhering of tears and lining can be carried out afterwards.



Figure 2

Strnad "Oberon", 1933, "Scheiterhaufenbild", No. 104047, watercolour, Chinese ink. Before treatment, raking light, 445 mm x 354 mm.



Figure 4
Strnad "Oberon", 1933, "Puck"
No. 107043, watercolour, Chinese ink.
Before treatment, raking light,
352 mm x 389 mm.



Figure 5
Strnad "Oberon", 1933, "Puck". After
treatment, raking light.



Figure 3
Strnad "Oberon", 1933, "Scheiterhaufenbild". After treatment, raking light.

5. Technical observation*

In order to understand the mechanisms of humidification involved when using the GORE-TEX (R) sandwich, it was necessary to measure the moisture content of the tracing paper during its humidification. This was achieved by measuring the electrical resistance of the tracing paper's surface, using an especially designed probe**. Preliminary tests showed that the moisture content of the papers inversely proportional to its electrical resistance.

Short-term measurements of up to one hour showed that there were no significant differences between humidifying with plain water or with an ethanol / water mixture as described above. It was observed that the electrical resistance falls rapidly during the first eight to ten minutes. After this period only a slow decrease of the electrical resistance could be detected. Fig. 6 shows such a typical curve, where the inverted electrical resistance is plotted against time. In this case it was assumed that the inverted electrical resistance is equivalent to the moisture content of the tracing paper.

Another interesting observation was made by measuring the exact dimensions of historic tracing papers before, during and after treatment. Increase in size was proved to be minimal (below 0.2 %) as illustrated in Fig. 7. This increase is partly the result of the flattening of creases during treatment (see Fig. 2-5).

Figure 6

Approximate moisture content of the tracing paper during humidification treatment in the GORE-TEX (R) sandwich.

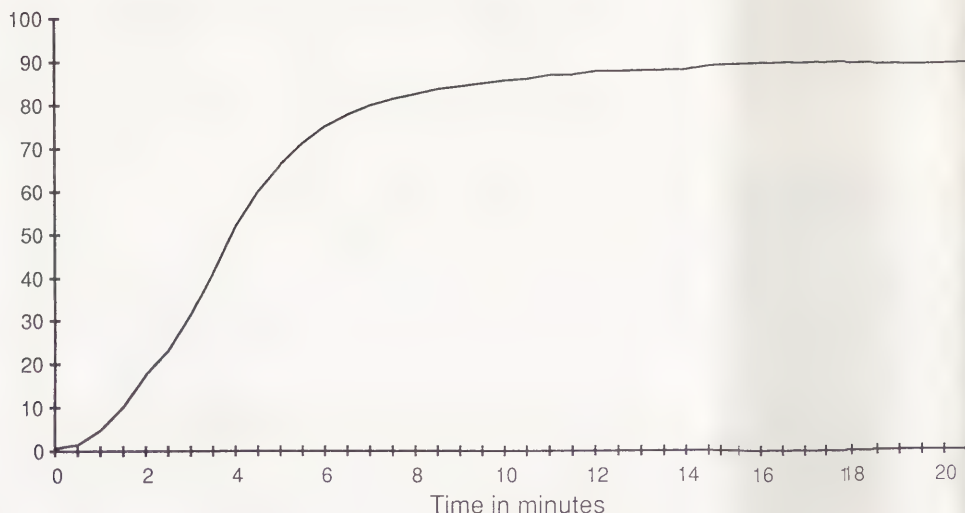
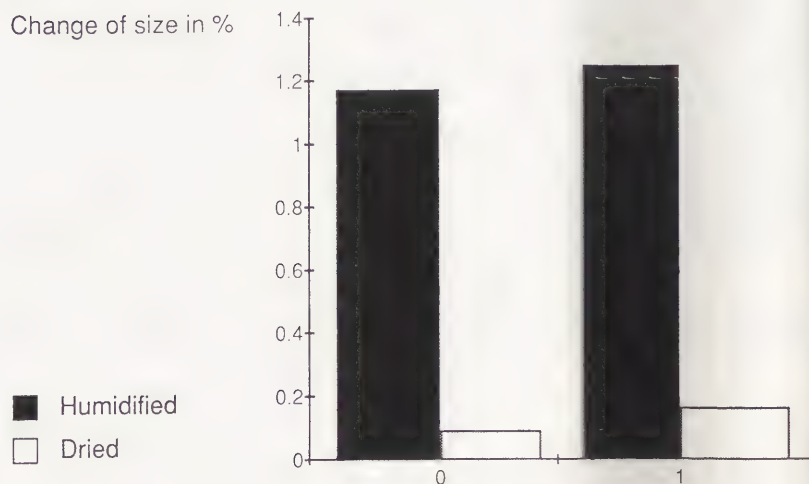


Figure 7

Change of size during and after humidification treatment in the GORE-TEX (R) sandwich, comparing humidification with water (0) and with a water/ethanol mixture (1).



* Please note that, due to the ongoing nature of these investigations, the following results are preliminary and not conclusive.

** This probe was designed and manufactured in collaboration with the company 'MICROTOOL' (R) in Graz, Austria, which also supplied a special constructed data ram to automatize the examination.

6. Conclusion

GORE-TEX (R) barrier makes it possible to humidify tracing papers in a very mild and controllable way. The slow relaxation results in minimal enlargement of the papers, which exhibit almost their original size after drying. When fully relaxed, even tracing papers with severe undulations can be flattened. The pressure of the suction table keeps the object flat until it is dry.

7. Materials and Suppliers

GORE-TEX barrier

W.L. Gore & Associates, Inc.
100 Airport road
P.O.Box 1550
Elkton, MD 21921
USA
(301) 392-4440

Viledon C 1974

100% polyester, non-woven fabric

Carl Freudenberg
P.O. Box 1369
D-6940 Weinheim
FRG
(201) 80-1

Melliphan

Fa. Wettlinger Kunststoffe
Neulerchenfelderstr. 6-8
A-1160 Wien
Austria
(222) 439-386

MICROTOOL

Hard- & Software-Entwicklung
Meß- & Regeltechnik
Josef Krainerstraße 42
A-8042 Graz
Austria
(316) 402-843

8. References

1. S.A. Yates, "The Conservation of Nineteenth-Century Tracing Papers", The Paper Conservator, Vol. 8 (1984): 20-39.
2. C. Steinkellner, "Transparentpapier" (Diplomarbeit, Meisterschule für Restaurierung und Konservierung, Akademie der bildenden Künste, Wien, 1978).
3. W.L. Gore & Associates Inc., Art humidification, Product Information, (Elkton, MD: W.L. Gore & Associates Inc., 1986).
4. K.M. Keyes, "Some Practical Methods for the Treatment with Moisture of Moisture-Sensitive Works on Paper" (Symposium 88, Abstracts, Talk: 6. 10. 1988, Ottawa, Ontario: Communications Canada/Canadian Conservation Institute 1988)
5. F. Flieder, F. Leclerc, C. Laroque, P. Richardin, B. Guineau, "Analyse et Restauration des Papiers Transparents Anciens", Les Documents Graphiques et Photographiques, Analyse et Conservation 1986-1987 (Paris: Archives Nationales, 1988) 93-139.

ABREGE

Le recensement des papiers peints en Italie a permis de mieux connaître et d'analyser systématiquement leurs conditions de conservation et de mettre en évidence les problèmes majeurs. Ceux-ci étant dus en grande partie aux différents systèmes de montage, une recherche a donc été entreprise dans cette direction pour sélectionner des produits mieux adaptés. Deux nouveaux adhésifs ayant subi les premiers tests de contrôle sont présentés:

Vinnapas-dispersion EAF 60 (R) et Vinnapas-dispersion AF 75 (R)

MOTS CLES

Papiers peints, recensement, conservation, montage, adhésif, Vinnapas-dispersion EAF 60, Vinnapas-dispersion AF 75.



Fig.1



Fig.2

RECENSEMENT DES PAPIERS PEINTS EN ITALIE - PROBLEMES DE CONSERVATION ET DE MONTAGE

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Depuis quelques années en Italie se manifeste un intérêt grandissant pour la sauvegarde des demeures historiques. Une association est née dans ce but (1); des congrès sont organisés au cours desquels sont présentés les problèmes relatifs aux arts majeurs comme les fresques, les peintures, les sculptures, mais aussi ceux relatifs aux arts mineurs et en particulier aux revêtements muraux moins connus, comme les tapis.

C'est dans ce contexte que l'attention des responsables du patrimoine se porte depuis trois ans sur la conservation et la restauration des papiers peints. La restauration des papiers de Dufour et Leroy, "les vues d'Italie", conservés au Palais d'Arco à Mantoue, voulue par le surintendant des beaux-arts de Mantoue, à l'époque Antonio Paolucci, a marqué le point de départ d'une recherche plus vaste et du renouveau de l'intérêt pour cette technique.

Pour faire une telle recherche en Italie, il était indispensable d'acquérir le plus d'informations possible sur les différents types de papiers peints existants et sur leur état de conservation. Nous avons commencé cette étude par la consultation de livres sur les palais, villas et demeures historiques des différentes régions italiennes puis par des contacts avec les surintendances aux beaux-arts et à l'architecture. Ces derniers nous ont communiqué de nombreuses adresses de propriétés privées et publiques, où sont encore conservés des papiers peints, ainsi que des indications bibliographiques très utiles.

Toutes ces informations nous ont permis de tracer une première carte de régions où existe le plus grand nombre d'exemples de papiers peints. Ainsi les régions du Piémont, de la Lombardie, de l'Emilie Romagne et de la Toscane sont les plus riches en papiers de toute sortes.

Les collections de dominos ou petits éléments de papiers peints recensés ou accessibles au public sont, en général, conservés dans les musées ou dans les bibliothèques et ne présentent pas de problèmes particuliers de conservation et de restauration.

Au Palais Pitti de Florence sont conservés des papiers chinois montés en petits éléments sous forme de tableaux. Certains sont actuellement en cours de restauration dans le laboratoire de l'Opificio delle Pietre Dure de Florence. Ils présentent un problème lié à la qualité du papier chinois, qui devient très fragile et friable comme du verre.

Pour mieux connaître les papiers chinois, panoramiques et papiers tentures conservés encore sur place, nous avons tout d'abord établi les contacts avec les propriétaires, puis effectué des visites. Nous avons ainsi pu recueillir une importante documentation photographique et des informations techniques sur les méthodes de conservation "in situ" des papiers peints.

Nombreux sont les exemples de papiers collés sur toile clouée soit directement sur le mur, soit sur des baguettes de bois fixées au mur. Les papiers chinois sont souvent montés ainsi. Nous avons aussi des exemples de panoramiques montés de cette façon.

Chez les antiquaires les panoramiques sont, en général, collés sur toile pour les rendre plus résistants aux différents transports et manipulations et permettre de les tendre sur châssis.

Certains papiers chinois ou panoramiques sont collés directement au mur, d'autres avec un papier intermédiaire.

Quant aux papiers tentures, imprimés ou veloutés, ils sont également collés soit directement au mur, soit avec un papier intermédiaire. Il en existe de nombreux exemples en Italie.

Pour tous ces papiers, qui présentent souvent des problèmes de déchirures et de décollement du mur, il est préférable d'agir sur place, en particulier lorsqu'il s'agit de papiers veloutés très délicats et sensibles à toutes manipulations.

Les problèmes communs à tous les papiers sont les suivants:

- la poussière, facilement éliminable par gommage avec de la poudre de gomme ou de la gomme mie de pain. (Fig.1)
- les infiltrations d'eau par les toits qui peuvent provoquer des dégâts irréparables et qui obligent au décollage complet et à la restauration des panneaux endommagés. (Fig.2)
- les fissures des murs, dues souvent à des mouvements de terrain, qui provoquent des déchirures sur les papiers; des témoins doivent être placés sur les fissures et l'intervention ne sera faite sur les papiers qu'au moment où les murs auront at-



Fig.4



Fig.5



Fig.7



Fig.3

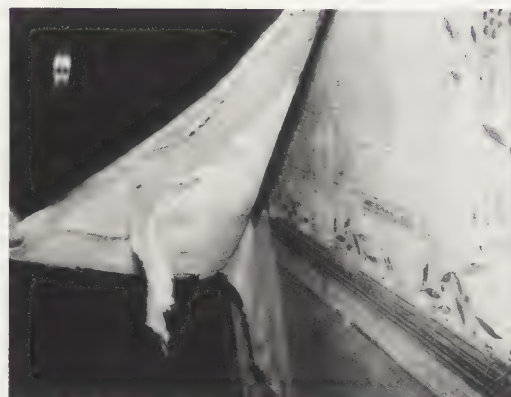


Fig.6

- teint une complète stabilité (Fig.3)
- le contact avec des murs externes humides (Fig.4)
- le décollement des papiers du mur à cause du vieillissement de l'adhésif (Fig.5)
- le mouvement des toiles de support qui provoque des différences de tension, des ondulations et quelquefois des déchirures
- le contact direct des papiers avec un plâtre mal préparé et irrégulier (Fig.6)
- les altérations de la surface dues au frottement (Fig.7)
- les anciennes restaurations faites suivant des critères et avec des matériaux peu adaptés à la restauration des papiers peints: utilisation de toiles très épaisses (lin et chanvre), colle de lapin, pâtes de farines mixtes, Vinavil pur, couleur à détrempe, etc. (Fig.8, Fig.9).

A partir de ces données et en tenant compte des expériences de restaurations déjà effectuées et publiées, nous avons pu mettre l'accent sur le problème central de la conservation de ces papiers, c'est-à-dire le remontage. En effet, lorsque les papiers ont besoin d'être décollés de leur ancien support ou du mur au cours d'une restauration ou lorsqu'ils sont déjà décollés, il faut trouver une technique de montage qui permette de travailler plus aisément sur ces grandes dimensions. Cette technique doit aussi permettre de résoudre les difficultés liées à l'irrégularité de la porosité des papiers et à la délicatesse des couleurs à la gouache. Nous avons donc, tout d'abord, défini les critères pour le choix des matériaux: support et adhésif.

support: toile de synthèse, de dimensions stables, à trame large et plate, légère, compatible avec l'adhésif

adhésif: application en couche mince discontinue, compatible avec les couleurs à la gouache, compatible avec la toile de support et le papier, applicable avec un solvant non aqueux et le moins toxique possible, et à une température qui ne dépasse pas 50°C

Comme il n'existe pas d'adhésif actuellement sur le marché qui réponde complètement à ces exigences, nous avons jugé nécessaire de prendre des contacts avec l'industrie qui travaille dans le secteur de la conservation. Nous avons établi une collaboration avec la société Syremont de Milan (2).

Sur proposition de cette société nous nous sommes orientés vers des polymères autocollants.

En d'autres termes, l'adhésion sera réalisée en appliquant une couche du produit en émulsion, de préférence sur un support intermédiaire en papier; lorsque le solvant sera évaporé et le film à pouvoir adhésif permanent formé, nous procéderons à l'adhésion par contact et légère pression.

Les adhésifs de ce type donnent lieu généralement à la formation de joints moyennement tenaces et donc théoriquement réversibles grâce à une action mécanique modérée.

Nous nous sommes orientés bien évidemment vers les produits autocollants sans plastifiant et donc plus fiables dans le temps.

Suivant l'indication de la société Syremont, nous avons soumis aux premiers contrôles expérimentaux deux produits à base acrylique de la société Wacker: Vinnapas-dispersion EAF 60 (R) et Vinnapas-dispersion AF 75 (R) (Ved. Matériaux). Ces produits, étendus sur une surface, produisent en un temps limité (15-30 minutes) un film à pouvoir adhésif permanent pratiquement incolore et stable.

Les tests de contrôle effectués au laboratoire de l'Opificio delle Pietre Dure de Florence avaient pour but de comparer les deux produits et de faire varier les temps de séchage du film avant l'adhésion, dans les deux cas de figure (toile seule

ou toile + papier) et de corriger la formulation des produits en ajoutant des charges ($\text{Ca}(\text{OH})_2$) pour tamponner la légère acidité. Nous avons voulu aussi vérifier le comportement de l'adhésif en l'appliquant sur le verso de l'objet plutôt que sur le support, ce qui est théoriquement préférable. Le tableau ci-joint donne le schéma des essais déjà effectués.

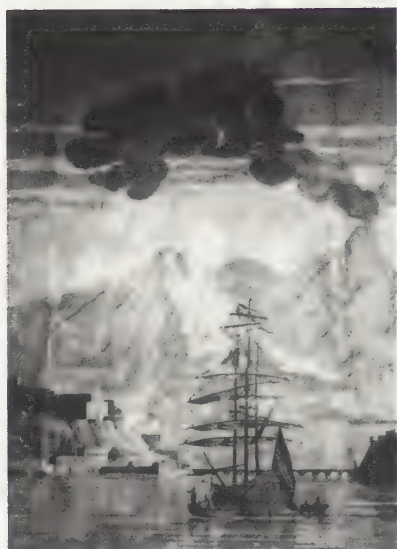


Fig. 8



Fig. 9

SCHEMA DES TESTS EFFECTUES

Temps de séchage	support papier	ADHESIF APPLIQUE SUR support toile	verso de l'objet
minimum	2 / EAF 60 2 / AF 75	- -	1 / EAF 60 1 / AF 75
1 h	3 / EAF 60 3 / AF 75	5 / EAF 60 5 / AF 75	4 / EAF 60 4 / AF 75

La première valeur indique le numéro du test, la seconde le sigle des produits expérimentés.

Tous les tests préparés en appliquant les adhésifs directement sur le verso de l'objet (1 / EAF 60, 1 / AF 75, 4 / EAF 60, 4 / AF 75) ont donné des résultats négatifs quant à la réversibilité. En effet, le décollage provoque souvent des déchirures sur l'objet en papier; l'action mécanique nécessaire est dans tous les cas traumatisante pour la couche picturale. En outre, le produit AF 75 (le plus liquide) tend à provoquer, lorsqu'il est appliqué directement sur l'objet, des taches et des auréoles dues à la migration du solvant.

Tous les autres essais avec les adhésifs appliqués sur support papier (2 / EAF 60, 2 / AF 75, 3 / EAF 60, 3 / AF 75) ont montré une réversibilité satisfaisante. Nous n'avons pas relevé, par ailleurs, de différences significatives de comportement en faisant varier le temps de séchage. En revanche nous notons des résultats différents selon les produits; l'EAF 60 en particulier, étant déjà plus dense, pénètre modérément, permet une plus facile réversibilité et ne provoque pas de taches. Les tests exécutés sur support toile se sont révélés négatifs car l'adhésif a tendance à pénétrer dans la trame du support au détriment de la formation du film, provoquant des inconvénients certains pour l'application (3). Pour une plus sûre sauvegarde de l'objet, et en particulier de sa surface picturale, nous avons voulu vérifier ces mêmes adhésifs appliqués sur le verso de l'objet pré-traité avec une couche fine de fixatif. Nous avons utilisé à cet effet un premier fixatif bien connu, le Klucel G (4), et un second, récemment expérimenté: FOMBLIN CO (5).

Bien qu'une expérimentation plus approfondie soit nécessaire, nous avons déjà constaté, en règle générale, une amélioration de la réversibilité due surtout à l'effet "écran" du fixatif qui limite la pénétration du produit dans les fibres du papier. Nous avons commencé actuellement une série de contrôles avec des cycles de vieillissement accéléré pour vérifier notamment la stabilité des propriétés physico-mécaniques de l'adhésif dans le temps.

Parallèlement à cette recherche, nous projetons d'organiser une exposition sur les papiers peints à Florence dans laquelle seront présentés en partie les résultats de cette étude.

Notes

- 1) Associazione Dimore Storiche Italiane, Corso Vittorio Emanuele II, 173 - 00186 Roma (tel: 06/6544553)
- 2) Syremont (Méthodes pour la conservation et la restauration) Via Camperio, 9 20123 Milano, Italie (tel: 02/62705477) telex: 310679 MONTEDI; Telefax: 02/62705413
- 3) L'impossibilité de formation d'un film adhésif bien défini entre objet et toile et la migration du produit à travers la toile elle-même peut provoquer la création d'une couche gluante externe difficilement réversible mécaniquement.
- 4) Hydroxypropylcellulose, Hercules Incorporated, 910 Market Street, Wilmington, Delaware 19899 USA (tel: 302-5755700)
- 5) Elastomère fluoruré, Montefluos (Groupe Montedison), Via Principe Eugenio 1/5, 20155 Milano, Italie (tel: 02/53331)

Matériaux

Wacker-Chemie, Italia SpA, Via Fantoli 21/13, 20138 Milano (Tel: 02/50981)
telex: 314060 WACKER; telefax: 02/5064605

Vinnapas-dispersion EAF 60

Le Vinnapas-dispersion EAF 60 est une dispersion à 60%, exempte de plastifiant, à base d'un terpolymère de vinylacétate-éthylène-ester de l'acide acrylique avec les caractéristiques suivantes:

- résistance à la migration du plastifiant
- densité $1.03 \pm 0.01 \text{ g/cm}^3$ (20°C)
- viscosité $2600 \pm 600 \text{ mPa.s}$ (20°C)
- pH ≈ 5.5
- température minimum de formation du film ($\approx 0^\circ\text{C}$)
- pouvoir d'adhésion élevé en surface

Vinnapas-dispersion AF 75

Le Vinnapas-dispersion AF 75 est un copolymère ester de l'acide acrylique, à 60% d'extrait sec, exempt de plastifiant, avec les caractéristiques suivantes:

- très bonne adhésion à basse température
- densité $1.00 \pm 0.01 \text{ g/cm}^3$ (20°C)
- viscosité 1.500 mPa.s (20°C)
- pH ≈ 5.5
- température minimum de formation du film ($\approx 0^\circ\text{C}$)
- pouvoir d'adhésion élevé en surface

Remerciements

Nous remercions pour leur collaboration les surintendances à l'architecture et aux beaux arts de Turin, Bologne et Florence ainsi que les mairies de Govone (Cuneo) et de Castell'Alfero (Asti), le Museo Civico de Bassano del Grappa, Renzo Mangili de Bergame et tous les collectionneurs privés. Nous remercions en particulier Monica Bietti de la surintendance aux beaux-arts de Florence pour ses informations provenant d'une recherche non publiée.

ABSTRACT

The restoration of prints from the archive of the "Wiener Secession" with foxing marks of biological origin made it possible to compare several bleaching methods. After preliminary tests three suitable bleaches were selected: Potassium permanganate, calcium hypochlorite and hydrogen peroxide. These procedures had to be adopted to the special requirements of the objects. The extraordinary intervention of bleaching should be carried out under conditions as safe as possible.

KEYWORDS

PAPER BLEACHING, POTASSIUM PERMANGANATE, CALCIUM HYPOCHLORITE, HYDROGEN PEROXIDE, FOXING, WASHING, DEACIDIFICATION.

BLEACHING OF FOXING STAINS IN ART NOUVEAU PRINTS

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1. Introduction

The goal of this study was to compare several usual bleaching methods on biologically caused foxing stains from the conservator's point of view. Conditions gentle for the paper as well as practical for the restorer had to be found. Prints from the archive of the "Wiener Secession"-supplements to the "Founder Editions" of "Ver Sacrum"- offered the possibility to make such a comparison. All 108 objects showed foxing marks from biological origin. As the prints had similar prerequisites concerning stains, paper quality, age and storage, parallels could be drawn among the results of different bleaches. Seven bleaching methods were tested and compared. On the basis of the results of these tests three suitable procedures were selected. For the special case of prints with foxing it was necessary to find favorable conditions concerning pre- and after-treatment, concentration, pH, bleaching time etc. The comparison was merely made from the conservator's point of view. The aim was to reduce the disturbing effect of the stains without bleaching to the total disappearance of the discolourations in a way that the paper showed an harmonious aged tone. The art object and not the stains should draw the attention of the spectator.

2. History

The treated prints are supplements to the "Founder Editions" of "Ver Sacrum". "Ver Sacrum" was the magazine of the Association of Fine Artists "Wiener Secession" appearing from 1898 to 1903. "Ver Sacrum" is the only German speaking art nouveau magazine which was founded by artists. To improve the uncertain financial situation a limited number of de luxe editions for sponsors was published. Signed prints were enclosed with the "Founder Editions". Numbers of these editions were produced only for the first and second annual volumes, 1898 and 1899 (1).

3. Condition

The paper of the prints - lithographs, wood-engravings and etchings - is mainly composed of cotton fibers and cellulose with admixtures of rags. The objects showed a high amount of surface dirt and discolouration. Foxing marks of differing intensity and shape disfigured all treated prints.

Under UV-light some stains fluoresced white to yellow, others appeared dark (2). The margins of some objects showed tears. Surface pH-measurements with non-bleeding indicator strips (Merck 9541, 9542) yielded values between 5.3 and 5.7.* (3)

* The pH measurements of the surface of a wetted paper can be considered as a spot test of hydronium ions (H_3O^+). The test provides information on acid compounds being present in the paper web and being able to migrate in the time of detection to the indicator. Surface tests can only be considered as relative measurements and can only be used in order to rank different papers or treatments as far as acidity is concerned. pH measurements on the paper surface were done using the following procedure:

- a: The paper is moistened with two drops of distilled water.
- b: A pH indicator strip (Special pH indicator strips by Merck: 9541, 9542) is pressed on the wetted surface by means of a glass plate.
- c: After exactly two minutes the pH can be evaluated by comparison of the moist indicator strip with the colour chart.

The water that is used to wet the paper is saturated with CO_2 , it is therefore a slightly acidic solution (pH 5.5-6). The reading is not related to the neutral point and the pH value represents a relative measurement.

According to positive tests for aluminum an aluminum-sulfate-rosin size can be supposed*. A lignin test carried out with phloroglucinol proved absence of groundwood pulp**

Some prints from 1898 are marked with coin stamps. All prints from this edition are covered with Japanese tissue paper. The tissue papers which are printed with diverse patterns showed surface dirt and discolouration.

The brightness of the paper and the stains were measured on all objects to determine the efficiency of the different bleaches***. On the advice of M. Hey, who supposed copper and iron to be the origin of the stains, tests on copper and iron were carried out****. All tests were negative.

3.1. Microbiological Investigations

The biological origin of the foxing marks present on the prints was proved by three methods:

3.1.1. Light Microscopy

After staining with cotton blue very few elements of fungal hyphae and spores were detected.

3.1.2. Surface Electron Microscopy

Material from foxing spots was fixed, critical point dried, gold plated and observed in a TEM electron microscope. The observations revealed crystalline deposits appearing as clusters (Fig. 1) or single crystals (Fig. 2). Within the area of those depositions ovoidal elements of a size of about $10 \times 7 \mu\text{m}$ were detected. By their shape and ornamented surface (Fig. 3) they can be clearly identified as fungal spores. In some cases even hyphal elements were found. The fact that only few elements of fungal mycelium are present is explained by the autolytic process hyphae undergo in the course of the ageing process, whereas spores as propagating cells do not.

3.1.3. Cultivation on Agar Media

Pieces of paper ($5 \times 5 \text{ mm}$) from foxing spots were placed on 2 % malt agar and cultivated at 25°C . With 75 % of the foxing spots investigated, *Aspergillus niger* was identified as contaminant. This coincides very well with the observations mentioned above. Conidial spores of *Aspergillus niger* are of the size and ornamented structure observed on the paper samples. *Aspergillus niger* is known to produce great amounts of citric acid, which are deposited as crystals. Taking into account that fungal spores are able to produce hyphae after a very long period of dormancy (dozens of years) as soon as humidity increases, the spores observed and the fungus isolated may well be one and the same, responsible for foxing.

* The test on aluminum was carried out with a solution of aurin tricarboxylic acid ammonium salt (called aluminion, test solution: 1 g/l H_2O) on a taken paper sample.

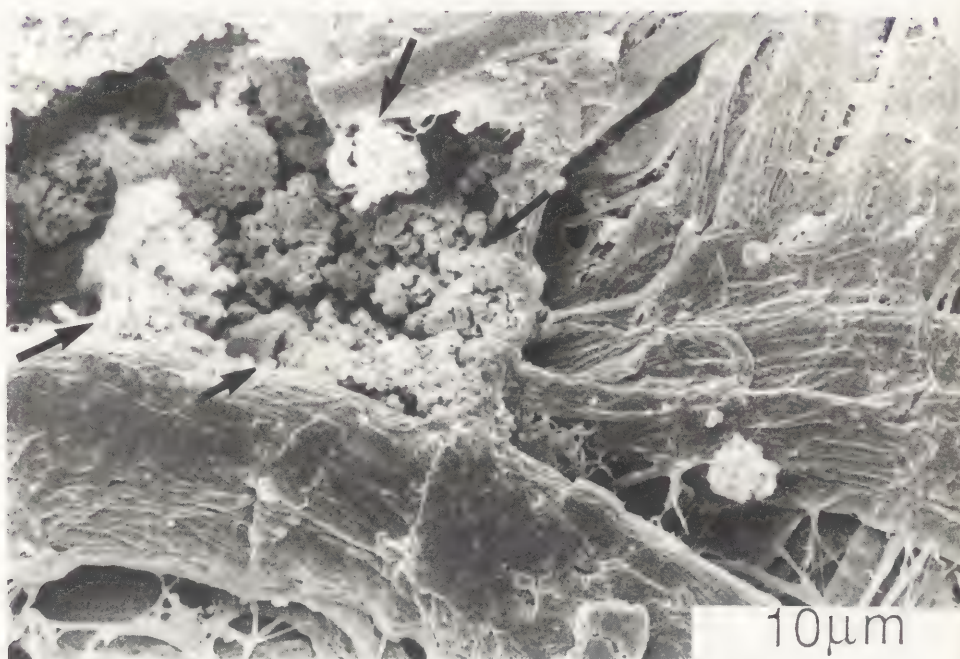
** The test for lignin was carried out with a solution of phloroglucinol and concentrated hydrochloric acid on a taken paper sample.

*** The brightness was determined with a FAG Vipdens 700P reflection-densitometer.

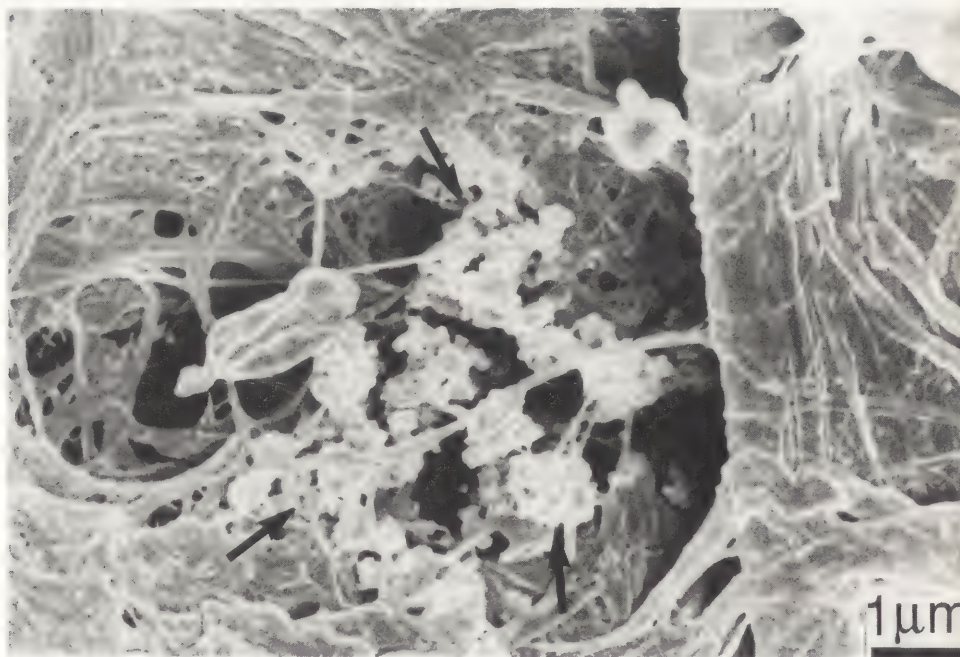
**** Merckoquant (R) 10003 copper test and Merckoquant (R) 10004 iron test were used to detect iron and copper. The foxing marks of some objects were washed with a solution of calcium hydroxide on blotting paper support on the suction table. The tests were carried out on the blotting paper on those spots where it had absorbed discoloured material from the foxing marks.

Figure 1

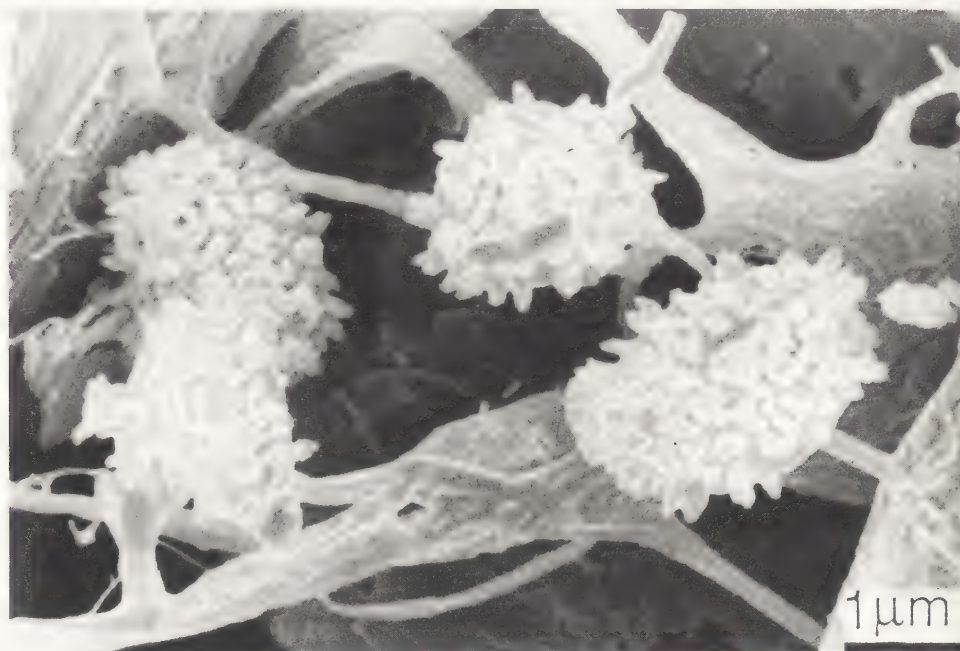
Crystalline deposits appearing as clusters on the paper in the area of foxing spots (arrows), SEM image.

**Figure 2**

Single crystals (arrows) on the paper in the area of a foxing mark, SEM image.

**Figure 3**

Typical fungal spores in the area of a foxing mark, SEM image.



4. Treatment

4.1. Washing, Deacidification

The Japanese tissue papers were removed by means of methylcellulose poultice. All objects were washed and deacidified following a procedure proposed by M. Hey (4, 5) that proved to be very successful:

- a: The paper is put in a water-alcohol bath, 1:1.
- b: The paper is rinsed in warm water for two hours. The water is changed every 30 minutes.
- c: The prints are deacidified in a calcium hydroxide solution for 30 min. (1 mg/l tap water, pH 9).

Before bleaching the paper was left to dry so that calcium hydroxide could react with CO_2 from the air to form calcium carbonate. The pH of the papers ranged from 6.5 to 7 (on the surface) after deacidification. The alcohol-water-bath greatly improved the efficiency of the washing procedure. In an alkaline bath, discolouration products are more easily dissolved. Calcium hydroxide is known to neutralize all acid compounds present. The reaction of unused calcium hydroxide to calcium carbonate forms an alkaline reserve in the paper which can neutralize acids being produced during bleaching and deactivate metal ions.

4.2. Tests

Seven usual bleaches were tested: Calcium hypochlorite, chloramine, chlorine dioxide, hydrogen peroxide, potassium permanganate, sodium borohydride and light bleaching (6). The results of these tests formed the basis for the selection of three methods with which the rest of the objects could be treated. Four prints were bleached according to each method. Potassium permanganate, calcium hypochlorite and hydrogen peroxide were selected. Potassium permanganate was used for prints with very dark stains, calcium hypochlorite for widespread discolourations and hydrogen peroxide for prints with few local stains.

4.3. Bleaching Procedures

4.3.1. Potassium Permanganate

Strong stains were bleached locally according to their darkness by means of a 0.25 % solution of potassium permanganate (pH 8) or a 0.5 % solution of potassium permanganate (pH 8). The bleaching solution was applied with a brush to the prewetted paper. In order to avoid bleaching haloes it is advisable to use a very thin brush and to wipe off excess solution. The point of the brush has to be placed exactly in the middle of the stain. Immediately or after a short time (30 seconds) the dabbed point was treated with 1 % potassium metabisulfite solution in order to stop the bleaching action and to avoid overbleaching. All locally bleached papers were rinsed in water.

Afterwards as a second step of the bleaching procedure an equalizing bath was carried out with a 0.1 % potassium permanganate solution:

1 g potassium permanganate + 1000 ml water = 0.1 % (pH 8)
Immersion time: 30 seconds

The prewetted papers were individually immersed in the solution for 30 seconds, taken out, dripped off and left to dry on blotting paper over night. The paper turned light brown. On the next day the objects were immersed in a 1 % potassium metabisulfite solution for 30 minutes. Subsequently the prints were rinsed in water for 2 hours. An alkaline bath in a calcium hydroxide solution (pH 9) for 30 minutes finished the treatment. Larger objects, 50 x 55 cm, were bleached locally and then a 0.1 % solution was applied with the brush. This was followed by an aftertreatment as described above.

Following this procedure overbleaching of the prints could be avoided. Residual manganese was totally removed as a result of the treatment with potassium metabisulfite and subsequent rinsing and deacidification (7). Elimination of manganese was clearly proved analyzing several original samples before and after treatment by means of atomic absorption spectroscopy (AAS).

4.3.2. Calcium hypochlorite

The stains were locally bleached with a 0.25 % solution (pH 11.5), dark stains with a 0.5 % solution (pH 12.5) according to the method previously described. The locally bleached prints were immersed in a bleach bath:

**1 g calcium hypochlorite + 2000 ml deionized water (0.05 %) Addition of calcium hydroxide solution to pH 10
Bleaching time: 10 minutes**

Immediately after the bleaching bath the objects were washed and then immersed in a 5 % acetic acid solution for 5 minutes. The prints were subsequently rinsed for 2 hours. An alkaline reserve was provided by a subsequent calcium hydroxide bath (pH 9) which was applied for 30 minutes.

4.3.3. Hydrogen Peroxide

The stains were locally bleached with varying concentrations according to the intensity of the discolouration: approximately 3 %, 6 %, 10 % and 15 %. The pH of the solutions was raised to 9 using a 25 % ammonia solution. The liquid was applied with a brush on the dry paper to avoid bleaching haloes. To even out the tone a 0.9 % solution was brushed on. One third of ethanol was added to reduce the risk of blistering (8):

**3 ml H₂O₂ 30 %
30 ml ethanol
67 ml distilled water
Addition of ammonia solution 25 % to pH 9**

After bleaching the papers were immersed in a 2 % sodium thiosulfate solution for 30 minutes. They were rinsed for 2 hours. An alkaline reserve step as described above completed the treatment. The tears were adhered with tissue paper and starch paste. All prints were resized with methylcellulose MC 400 (1 % solution). The dry prints were slightly moistened and left to dry between Viledon (R) (thermal bound polyester fleece, 100 % polyester) and blotting paper weighted with a glass plate.

5. Conclusion

The pre-treatment (alcohol-bath-washing-deacidification) resulted in a considerable reduction of the discolouration (9). As a consequence the concentration of the bleaches could be lowered drastically.

An agreeable even tone could be achieved with potassium permanganate, calcium hypochlorite as well as with hydrogen peroxide. The results of all three methods were similar with few exceptions. This means if the paper turns too white it is mainly caused by the bleaching conditions.

Washing, deacidification and resizing should follow every bleaching procedure.

These results are not applicable in all instances of bleaching. They refer to the special case of biologically caused foxing. The concentrations described cannot be used for all objects because the different nature of objects makes it impossible to state general bleaching methods.

Acknowledgement

This study was carried out as a qualifying diploma in conservation at the Academy of Fine Arts in Vienna. All practical and theoretical work was done at the workshops of the National Library. Authors are grateful to the Director of the National Library Dr. Magda Strebl for her support.

Authors thank Prof. Dr. Edelbert Köb, President of the Wiener Secession, for making numerous prints from the archives of the Secession available for this study.

Materials and Suppliers

Viledon C 1974
100% polyester fleece

Carl Freudenberg
P.O. Box 1369
D-6940 Weinheim
FRG

References

1. C.M. Nebel, Ver Sacrum 1898-1903 (Munich: 1979).
2. C.E. Cain, B.A. Miller, "Photographic, Spectral and Chromatographic Searches into the Nature of Foxing", AIC, 10th Annual Meeting, Preprints (Milwaukee: 1982), 54-62.
3. G. Banik, Instructions for Surface pH-Measurements on Paper Objects, Handout, SPC Course ICCROM, 1988,1989.
4. M. Hey, "Paper Bleaching: Its Simple Chemistry and Working Procedures", The Paper Conservator, Vol. 2 (1977): 10-23.
5. M. Hey, "The Washing and Aqueous Deacidification of Paper", The Paper Conservator, Vol. 4 (1979): 10-23.
6. H. Burgess, D. van der Reyden, K. Keynes, "Bleaching", in: Paper Conservation Catalog, 6th Ed. AIC Book and Paper Group, Washington DC, 1989.
7. A. D. Baynes Cope, "The Effect of Residues of Manganese Compounds in Paper on the Bleaching of Prints etc.", The Paper Conservator, Vol. 2, (1977): 3.
8. D. Clement, "The Blistering of Paper during Hydrogen Peroxide Bleaching", Journal of the AIC, vol. 23(1) (1983): 47-62.
9. K. Keyes, "Alternatives to Conventional Methods of Reducing Discolouration in Works of Art on Paper", in: Conservation of Library and Archive Materials and the Graphic Arts, G. Petherbridge Ed., Butterworths, London (1987): 49-55.

ABSTRACT

Biological analysis of a new efficient method using small doses of formaldehyde for mass document disinfection is given. The method is intended to prevent or control the growth of mold on documents damaged by water during disasters. Disinfection processes allow reducing the extent of air and document contamination in storages at an early stage of fungi development. The disinfection processing eliminates the epidemic danger for documents and for personnel.

KEYWORDS

Book storages, decontamination, epidemic danger, formaldehyde, fungi growth, mass processing.

MASS PROCESSING OF DOCUMENTS FOR FUNGI CONTAMINATION CONTROL

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A rise in the air humidity and correspondingly an increase in the equilibrium moisture content of materials constituting books occurs always whenever document storage conditions in libraries, archives and museums have been disrupted, and in various kinds of emergency situations. The unavoidable effect of such wetting of documents is the growth of mold which, at the standard temperature of 16 to 20°C and relative air humidity of 55 to 60 per cent, occurs within 48 to 72 h. When the premises' temperature is below 10°C, mold growth processes are considerably slowed down, but such storage conditions at lower temperatures cannot be always obtained, as well as a far more effective safe-keeping at the temperature of 4°C. No doubt, the most correct method of rescuing documents in such cases would be freeze drying; it, however, does not always save the situation: the process goes on sufficiently slowly and not on the scale comparable with the disaster that has occurred.

Thus, books that have been wetted release water into the surrounding air, which causes air humidity to fluctuate. Fungi grow while humidity equilibrium takes place. There are many cases known all over the world when mass contamination of library stocks was caused by the use of water for fire fighting. Moreover, methods of air drying applied, and the creation of powerful currents of hot air usually facilitated the spreading of fungi spores and the contamination of all the documents, including those that have not been wetted. Such a situation leads without doubt to a danger to the health of people as higher air contamination causes allergic skin and lung disorders in some people.

In this situation an investigation of the air in storage premises is carried out by sampling by means of the inertia method. To do so, the air is pumped through a narrow slit and hits the hard surface of the agar in a rotating Petri dish. Fungi spores, setting on the agar, are grown at the temperature of 28°C. Knowing the time they were sown by the air current, the speed of the air current and the number of spores that have germinated, it is easy to count their content in 1 cu.m of the storage air. After the fire at the Library of the USSR Academy of Sciences they proved to be from 80-100 to 5000 in 1 cu.m. Normally the spore content in the storage air does not exceed 800 to 1000. Thus, an "epidemic situation" was established in storages; the level of fungi contamination of the air, wall surfaces, shelves and documents themselves exceeded permissible standards.

In order to rescue library books and other documents and to prevent possible diseases of people it is necessary to decontaminate not only the books, but also the library rooms. From the viewpoint of library practice and saving labour the most rational seems to be disinfection of the entire storage along with the books. Decision in this case depends on the location of the library and the scale of the work required.

There are not less than 18 various known methods of chamber disinfection, but very few of them can be used with respect to all parts of storage rooms. First to be considered is the matter of how toxic are the agents to be applied and whether it is possible to use them in city conditions, in housing estates full of people. In particular, sanitary inspection departments in cities held inadmissible the use of methylene bromide and ethylene oxide.

The most reliable agent to begin the contamination of any objects is formaldehyde. Its water solution, commonly known as formalin, contains 40 per cent of formaldehyde. The application of formaldehyde to destroy pathogenes of human infections diseases and pathogenes of book diseases goes far back in history. This preparation has been repeatedly employed in libraries, museums and archives, and its advantages and disadvantages have been considered in detail. Formaldehyde has an insufficient penetration capacity, and there is a hazard of its explosion in certain conditions. It is also well-known that higher humidity and temperature contribute to the enhancement of its properties

as a biocide. Taking into consideration these and some other circumstances a variety of different methods of disinfection by formaldehyde fumigation in libraries, museums and archives have been elaborated and employed.

Having been assigned the task of decontaminating the storages holding over 10 million books, after the fire in the Library of the USSR Academy of Sciences, the authors made use of a new method of formaldehyde fumigation. Its principal distinctive features were that formalin was sprayed through jets, turning it into aerosol, along with the introduction of carbon dioxide at the temperature of 30°C as a retarder reducing explosion hazard. Before applying these chemical compounds the storages were hermetically sealed, warmed by air heaters up to the temperature of 45°C, and the air was humidified by spraying water up to the level of relative humidity of 88 to 92 per cent. This helped to get fungi spores out of the latent condition, to cause their germination, which in turn made it possible to achieve a lethal effect with lower concentrations of formaldehyde.

All these works were preceded by the setting up of a mycological control over the storages and disinfection process. To do so, test objects were places in books in different parts of the storage room. They were made of sterile filter paper strips inoculated with spore suspension. Test cultures for its making were fungi found most commonly on books and having sufficiently fast growth rate: *Aspergillus flavus* Lk. ex Gray and *Trichoderma viride* Pers ex Gray, isolated from contaminated books. These fungi possess a broad spectrum of fermentative activity, grow easily on different book materials and are distinguished by their strong resistance to biocides.

The spore suspension was made in sterile distilled water of a seven days old fungi culture grown on malt agar at the temperature of 28°C. The suspension was applied 0.1 mm in depth on 20 by 150 mm - wide paper strips then they were slightly dried and put in sterile paper envelopes. The test strips were placed equally over the entire space of the storage room taking into account a massive content of books in it and also the distance from the point where the gas mixture was injected. The test strips were taken out of the storage and put in sterile envelopes over a period of several days with 12 to 48 h intervals. Further, they were placed on the malt agar surface in laboratory conditions. The survivability of spores was determined visually by the early growth of mycelium and the colonial mat formation. It occurred after 48 to 72 h for negative results.

The efficiency of disinfection was expressed in percentage in accordance with the number of test strips with germinating spores. The exposure was interrupted after 90 to 100 per cent efficiency has been achieved on the surface of books. One case of data reading with a 24-hour exposure is shown in Table 1. It follows from Table 1 that a 24-hour exposure with the given formaldehyde content proved to be inadequate for the decontamination of inner surfaces of books.

Table 1
Decontamination efficiency depending on test strips location

Serial number	Formaldehyde in g/cu. m	Efficiency in per cent		
		on the surface of books and in the air		inside the books
		for <i>A. flavus</i>	for <i>T. viride</i>	
1	24.70	90.5	100	66-70
2	21.04	88.8	100	45.5
3	25.04	66.6	100	25

Further control for the process found some more dependencies which can be provided by analyzing Table 2 data, which contains the characteristics of processing three book storages. The examination of test strips shows that the greatest effect on the decontamination result depends on the exposure time of formaldehyde and its dosage per 1 book. Thus, in particular, if one compares case 1a and 2a, it will become clear that the exposure time is not compensated by the formaldehyde amount. In case 2a the dose is considerably high than that in case 1a, but when the time is reduced by two, the efficiency is twice as low. An increase in the exposure time, however, almost equalizes the results in case 2b. Particularly significant is the exposure time for decontamination of the inside of books. In case 3 the rooms are smaller than those in case 1b, formaldehyde is released twice as much in conformity with the number of books. With the same exposure time the results are nearly equal.

Table 2
Results of decontamination processes in three library storages

Characteristics of the process	Serial number					
	1		2			3
	a	b	a	b	c	a
Rooms space in cu.m	4568		5070			3640
Number of books	749435		674283			1300000
Number of books in 1 cu.m	164		132			357
Formaldehyde concentration in g/cu.m	21.04		36.70			50.64
quantity per 1 book in g	0.13		0.28			0.14
Exposure time in h	24	92	12	24	150	92
Efficiency in per cent						
T. viride on books						
- outside	82.2	100	57	93.8	92.9	92.1
- inside	-	42	25	33	66.6	50
A. flavus on books						
- outside	88.8	100	87.5	94.7	100	100
- inside	-	50	-	-	-	71

Now turning to Table 3 one can see that as formaldehyde goes on acting, absorbed by the books, their contamination continues to decline, whereas before the processing it continuously increased. That is why in the case under consideration it was important to eliminate the epidemic, to retard the mold growth on the outside of book bindings that just started, and to reduce the amount of spores on the books and in the air. The right side of the table, showing the condition of books after the decontamination, proves the efficiency of the process executed. The truth of this conclusion is supported also by the air examination data, taken in the storage which can now be entered. They are given in Table 4.

Table 3
Contamination of documents with fungi spores

Tier	Number of rooms	Contamination before disinfection in per cent			Contamination after disinfection in per cent	
		15 days before	10 days before	5 days before	1 day after	10 days after
1	5	33.3	60	80	11.1	0
2	5	50.0	66.6	95	12.5	0
3	5	66.6	70	100	7.5	2
4	5	60	83.3	85	14	2
5	5	60	90	87.5	7.5	4
6	4	62.5	75	95	12.5	6
7	2	35	75	73.7	12	0
8	3	40	40	70	13.3	2

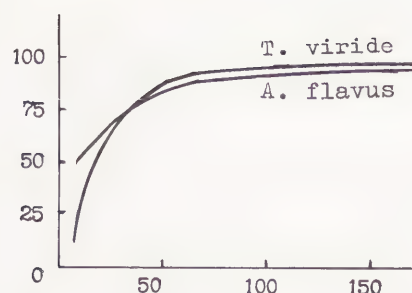


Fig. 1. Efficiency dependent on disinfection time tested by two fungi cultures.
Abscissa: time, h.
Ordinate: efficiency, %.

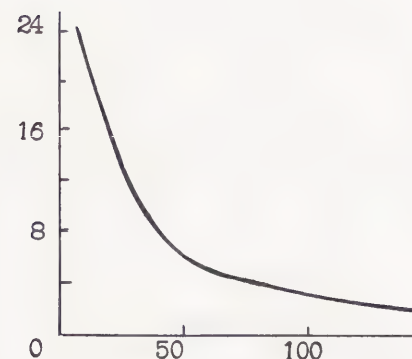


Fig. 2. Change in the formaldehyde concentration in air with disinfection time.
Abscissa: time, h.
Ordinate: concentration, mg/cu.m.

Table 4

Fungi spore content in storage rooms according to inertia method

Disinfection	Number of spores in 1 cu.m of air in tiers							
	1	2	3	4	5	6	7	8
Before	1750	900	296	1120	385	1390	560	1000
After	70	70	30	100	75	40	20	25

Thus, the fungi removal from air reached 92 to 93 per cent on average. These data were obtained as the processing was being carried out in storages of each tier. When the entire job was completed, the spore content in no rooms exceeded 20 to 60 per 1 cu. m. By prolonging the processing we achieved the condition in which the efficiency of disinfection of the inside of books reached 80 to 90 per cent.

After these results have been obtained, 20 per cent ammonia was sprayed also through jets in an equivalent quantity, which provided its reaction with formaldehyde in the air. Then one could enter the rooms without a gas mask and overalls. It was in the books that formaldehyde continued to act.

The curves (Fig. 1 and 2) show the conjugation of the biocide action and the absorption of formaldehyde by documents. It follows from Fig. 1 that differences in the formaldehyde action on fungi of two species is occurred only at the beginning of processing. In 24 hours the efficiency of action on the two

fungi equalizes and reaches its maximum in 150 hours. Within the same time periods (Fig. 2), the content of formaldehyde in the air decreases owing to its absorption by documents, which leads to a rise in the efficiency of processing. Thus, the fungi killing results are in direct proportion to the formaldehyde amount absorbed by documents.

As a result of the work done we succeeded in finding an efficient method of decreasing the contamination level of the air in book storages and documents kept in them at an early stage of their damage by fungi. The application of this process makes it possible to remove an epidemic situation both for the documents and the personnel.

RESUME :

Après avoir passé en revue les différents matériaux entrant dans la composition des produits d'enduction des papiers calques anciens, nous avons montré, pour un certain nombre, qu'il était possible de les mettre en évidence dans des microprélèvements d'échantillons anciens. En effet, la nature des produits, obtenus pour chacun d'entre eux avant et après dégradation, permet de les identifier par CG/SM en fragmentométrie sur certains ions caractéristiques. Une modélisation a été réalisée sur des papiers «calques» enduits selon les procédés anciens et vieillies artificiellement. Ces résultats ont permis l'étude d'une soixantaine de papiers transparents anciens, localisés et datés de 1800 à 1950.

Mots clés : CG/SM, papiers transparents, résines naturelles, produits d'imprégnation.

ANALYSE PAR CG/SM DES PRODUITS D'IMPREGNATION DE PAPIERS CALQUES ANCIENS

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Le but de ce travail est la mise en évidence et l'analyse des différents constituants utilisés pour la fabrication des papiers transparents anciens. Dans une étude précédente [1], après une revue bibliographique importante sur les recettes anciennes, nous avons commencé l'expérimentation par l'analyse de certains de ces produits d'imprégnation. D'après les textes, les produits les plus fréquemment employés pour rendre les papiers transparents sont répartis en trois catégories bien distinctes : huiles végétales (huile de lin, de ricin, de noix ou de noisette), résines naturelles (résine de pin, colophane, sandaraque, dammar) et cires naturelles (cire d'abeille). Seules les différentes huiles avaient été analysées par chromatographie en phase gazeuse (CPG) et chromatographie en phase gazeuse/spectrométrie de masse (CG/SM). Nous avons ainsi étudié une dizaine d'échantillons anciens.

Ce travail a été poursuivi par la caractérisation des résines et cires naturelles par CPG et CG/SM, ainsi que d'éventuels composés caractéristiques de leur dégradation. Parallèlement, nous avons fabriqué des papiers transparents selon différents procédés avec des huiles, résines ou des mélanges des deux puis analysé les extraits obtenus avant et après vieillissement artificiel. Ces résultats ont permis de caractériser une soixantaine de papiers calques anciens d'origines diverses.

ANALYSE DES RESINES UTILISEES DANS LES RECETTES ANCIENNES

L'analyse des résines naturelles a donné lieu à une très abondante littérature scientifique et de nombreux chercheurs en ont appliqué les résultats [2,3]. Une monographie relativement récente de J.S. MILLS [4] nous a permis de confirmer nos résultats ou d'ajouter quelques précisions. Si certains auteurs [5] préconisent l'emploi de la spectroscopie infrarouge, nous avons abandonné cette technique, en raison de l'absorption trop intense de certains composés, même présents en faible proportion, qui masque les autres matériaux.

Notre but étant d'analyser les produits extraits de calques, nous avons préféré utiliser la CG/SM qui s'avère très efficace pour la recherche de traces, surtout si on travaille en fragmentométrie. En effet, nous avons essayé, pour chaque famille de terpènes étudiée, de proposer une méthode simple de mise en évidence par sélection d'ions par SM. Afin d'analyser ces échantillons par CPG, nous les avons méthylés au diazométhane (CH₂N₂), qui réagit rapidement et avec de bons rendements.

Si les composés présents dans les huiles sont très simples à étudier par CG/SM, les spectres de masse des acides gras et de leurs produits de dégradation étant très connus, ceux présents dans les résines, en particulier les acides résiniques, sont beaucoup plus délicats à identifier, malgré une littérature abondante [6-14].

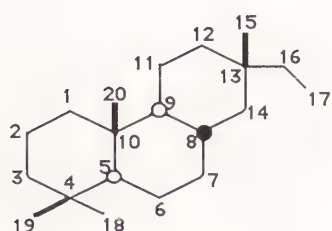
Résine de pin

Les résines de pin sont des oléo-résines, secrétées par diverses sortes de conifères. Nous avons étudié la résine de pin des Landes, recueillie sur plusieurs variétés de *pinus*, en particulier le pin maritime.

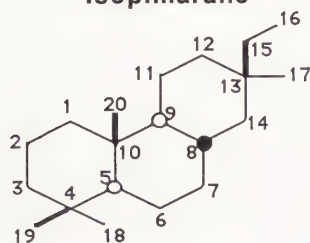
Le chromatogramme de la résine de pin brute (Voir fig.1) présente sept pics principaux identifiés avec d'une part leur temps de rétention [14], compris entre trente et trente cinq minutes, et d'autre part avec leur spectre de masse. Ce sont tous les esters méthyliques d'acides diterpéniques qui peuvent être répartis en trois classes en fonction du diterpène saturé dont ils sont dérivés. Ils sont de type isopimarane [acide isopimarique (IPM) et sandaracopimarique (SPM)], pimarane [acide pimarique (PIM)] ou abiétane [acide palustrique (PAL), déhydroabiétique (DAB), abiétique (ABT) et néoabiétique (NAB)]. L'ordre d'élution (PIM, SPM, IPM, PAL, DAB, ABT et NAB) est bien conforme à celui donné par ZINKEL [14] sur une colonne apolaire.

En début d'analyse, éluent des monoterpènes légers (d-longifolène (LONG) et un isomère du caryophyllène, le bicyclo [7.2.0] undécène-4 triméthyl-4,11,11 méthylène 8 (BUND)) et en fin d'élution, huit produits minoritaires dont l'acide 7,13,15 abiétatriénoïque (ATR).

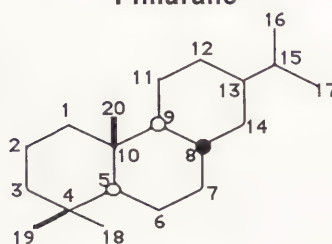
Une quantité d'environ 10 mg de résine de pin a été vieillie dans une étuve sèche à 80°C pendant plusieurs semaines. Les chromatogrammes obtenus sont comparés avec celui de la résine témoin. Par ailleurs, des essais de vieillissement photochimique ont été réalisés, mais les résultats sont similaires, avec cependant un taux d'avancement de la réaction beaucoup plus faible.



Isopimarane



Pimarane



Abiétane

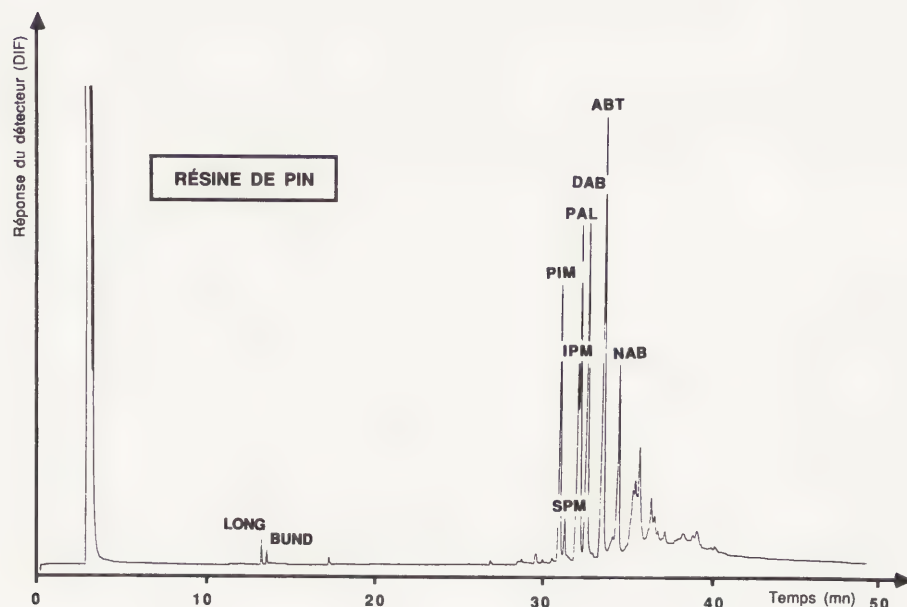
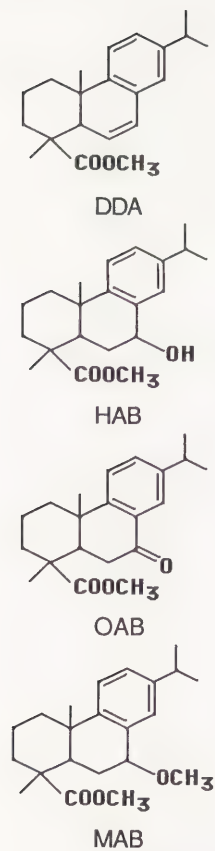


fig.1-chromatogramme de la résine de pin méthylée

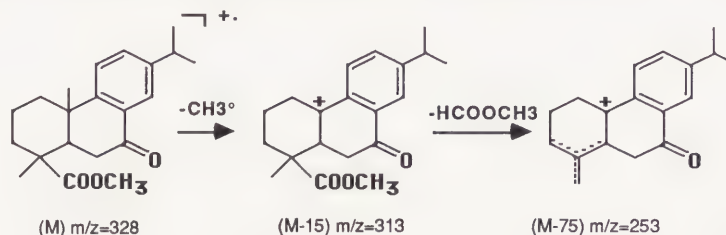
Pour la résine vieillie, on observe une évolution rapide de la nature et des quantités relatives des acides résiniques présents. Si les acides pimariadiéniques sont stables thermiquement, il n'en est pas de même pour les acides abiétadiéniques, qui tendent à s'aromatiser puis à s'oxyder. En effet, PIM, SPM et IPM restent dans les mêmes proportions que dans la résine de départ. Par contre, les acides abiétadiéniques PAL, ABT et NAB tendent à disparaître et DAB devient très vite le constituant majoritaire. MILLS [4] suppose que les acides PAL et NAB se transforment dans un premier temps en acide ABT, ce dernier se déhydrogénéant ensuite pour donner du DAB, beaucoup plus stable en raison de la présence du cycle aromatique.

Des composés nouveaux de type abiétique apparaissent, comme l'acide déhydro-7, déhydroabiétique, que l'on notera DDA, qui élué dans le pic du DAB, et un certain nombre de produits d'oxydation, dérivés oxygénés en position 7 du DAB, comme l'acide 7-hydroxydéhydroabiétique (HAB), l'acide 7-oxodéhydroabiétique (OAB) ou bien l'acide 7-méthoxydéhydroabiétique (MAB), dans l'ordre d'élué.

Les acides DDA, DAB et OAB deviennent les pics principaux du chromatogramme après quelques semaines de vieillissement. La présence simultanée de ces trois acides dans un même échantillon est la condition nécessaire et suffisante pour l'identification d'une résine de type résine de pin. La recherche sélective par fragmentométrie des ions principaux obtenus en impact électronique (IE) permet de les mettre en évidence avec une excellente sensibilité. Les ions 237, 239 et 253 sont les pics de base des spectres de DDA, DAB et OAB respectivement. Dans chacun des cas, cet ion, de masse $M-75$ par rapport à la masse moléculaire M de l'acide, correspond à la perte du groupement méthyle du carbone C20, suivie de la perte de la fonction ester avec transfert d'un hydrogène [7,11]. Nous donnons le mécanisme proposé pour l'OAB :



Acides triterpéniques



Colophane

Le résidu solide résultant de la distillation de la résine de pin mélangée à de l'eau, est un mélange complexe dans lequel on trouve la colophane, isolée directement par élimination de l'eau par chauffage. La composition de la colophane ainsi obtenue dépend naturellement de la résine de pin de départ.

Comme pour la résine de pin, les pics principaux sont les sept acides cités plus haut (PIM, SPM, IPM, PAL, DAB, ABT et NAB) avec quelques différences de proportion. Notre étude n'a pas donné lieu à des analyses quantitatives mais on peut remarquer, comme l'avaient supposé certains [4], que la proportion relative de PIM et SPM reste constante et la même que pour la résine de pin d'origine. Les monoterpènes et les composés plus lourds, décrits précédemment, sont présents mais en plus faible quantité.

On remarque que colophane et résine de pin vieillissent de façon similaire, ce qui est logique étant donné leur composition très proche. Cependant, la colophane semble se dégrader moins rapidement, mais cela résulte de son état de dégradation moins avancé au départ de l'étude. La distinction colophane / résine de pin est donc impossible dans un échantillon ancien, mais leur mise en évidence par SM s'effectuera par sélection des trois ions : 237, 239, 253.

Essence de térébenthine

L'essence de térébenthine, obtenue par distillation de la résine de pin en présence d'eau, est constituée d'un mélange complexe de monoterpènes de formule générale $C_{10}H_{16}$ dont le produit principal est l' α -pinène (de 50 à 70%) accompagné du β -pinène (de 20 à 25%). Des traces des acides résiniques (PIM, SPM,...) de la résine de pin éluent en fin d'analyse. Employée comme solvant dans la fabrication de certains papiers transparents, elle va presque totalement s'évaporer après séchage du papier. C'est pourquoi nous ne l'avons pas étudiée.

Sandaraque

La résine sandaraque est le produit du *callistris articulata* ou *thuya articulata*, qui croît en Afrique du Nord. Deux résines ont été analysées et nous avons constaté qu'elles étaient très différentes l'une de l'autre, non pas en ce qui concerne la nature de leurs constituants mais plutôt dans leur répartition.

Comme l'indique son nom, la résine sandaraque contient une forte proportion de SPM et d'acide 12-acétoxy sandaracopimarique (AcSPM). Ce sont les principaux constituants de la première résine analysée.

Celle que nous avons utilisée pour la suite de notre travail possède une forte quantité d'essence, constituée d' α et de β -pinène. Les deux acides pimaradiéniques ne sont plus les constituants majeurs mais sont accompagnés d'autres diterpènes de type labdane. On trouve ainsi des alcools (manool (MAN)), des monoacides (acide communique (COM), éluant dans le pic SPM) et des diacides (acide athécique (ATM), déhydroathécique (LDA) et pinifolique (PIN)).

Après dégradation à 80°C, on remarque peu de changement dans la nature des acides résiniques en dehors d'une disparition immédiate de COM. Après trois semaines de vieillissement, les cinq pics principaux sont : SPM, PIN, LDA, AcSPM et ATM. Les spectres de masse en IE de ces diterpènes possèdent une caractéristique très intéressante : l'ion 121 est toujours pic de base.

Il correspond, pour les trois acides de type labdane (PIN, LDA et ATM), à l'ouverture du cycle B, suivie de la perte de la chaîne latérale, par un mécanisme de réarrangement à six centres. L'ion formé perd alors facilement son groupement fonctionnel pour donner l'ion 121 [9] comme pour LDA (Voir fig.2).

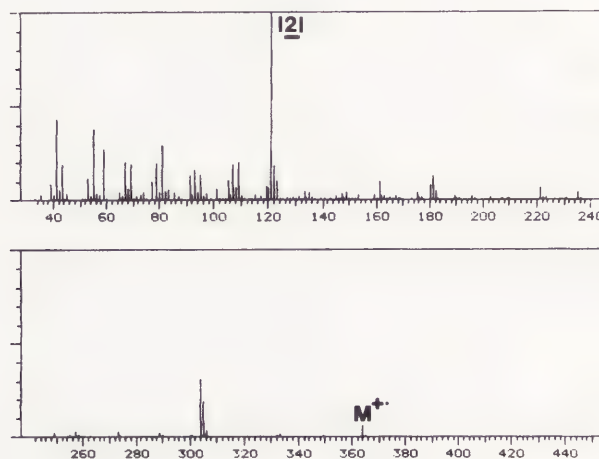
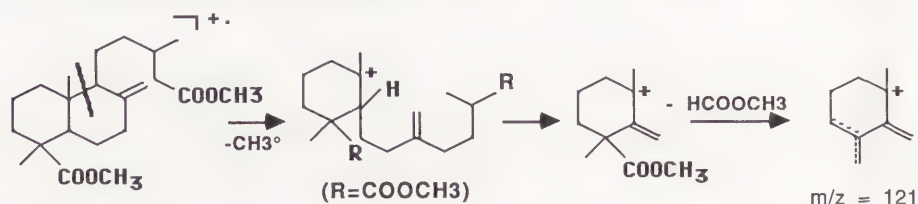


fig.2-spectre de masse en impact électronique du déhydroathécate de méthyle
Pour les acides SPM et AcSPM, l'ion 121 provient d'une fragmentation selon un mécanisme analogue [7]. Ainsi, la recherche sélective de cet ion 121 donne une empreinte similaire au courant ionique total (acquisition de l'ensemble du spectre) et permet, dans un échantillon inconnu, de révéler la présence de sandaraque.

Cire d'abeille

Cette cire animale a été très longtemps utilisée dans la fabrication des papiers cirés. Alcanes et acides gras saturés constituent la majeure partie des produits libres de la cire d'abeille. Les alcanes présentent une répartition gaussienne, en commençant du heneicosane (n-C21) au tétratriacontane (n-C34) avec un maximum pour le heptacosane (n-C27). De même, les acides gras sont à nombre pair d'atomes de carbone, et leur distribution passe du C22:0 au C32:0 avec un maximum pour le C24:0. C'est un produit naturel connu pour sa stabilité thermique. Des études sur son vieillissement à long terme n'ont pas montré de modification importante dans la composition de sa fraction soluble. L'identification de la cire d'abeille est facile par SM. La somme des ions 74+87 permet de mettre en évidence les esters méthyliques d'acides saturés. Il suffit de vérifier la répartition gaussienne des acides gras lourds (>C20:0), et surtout la prédominance du C24:0, par recherche de l'ion moléculaire $m/z=382$. Les alcanes sont souvent les pics principaux dans la cire d'abeille et leur recherche est plus aisée.

Résine dammar

La résine dammar est une résine recueillie principalement en Malaisie et en Indonésie. Celle que nous avons étudiée est constituée d'une faible fraction sesquiterpénique et d'une fraction triterpénique. En raison des masses moléculaires importantes de ces triterpènes, nous avons augmenté la pression du gaz vecteur à 0,8 bar. Les triterpènes (Voir fig.3) sont de type dammarane (dammaradiénone, dammaradiénol, hydroxydammarénone, dammaréniol et acide dammarénolique), oléane (acide oléanolique et acide ursonique) ou hopane (hydroxyhopanone). Ces résultats sont conformes à ceux donnés par De La Rie (R.) [15], qui a montré [16] également l'apparition de triterpènes de type ocotillane, comme l'acide shoréïque, au cours du vieillissement. Le spectre de masse de ces composés présente un ion 143, toujours pic de base en IE, accompagné des ions 125 et 107. Ainsi, la résine dammar peut être mise en évidence dans un échantillon ancien par sélection de la somme de ces trois ions : 143+125+107.

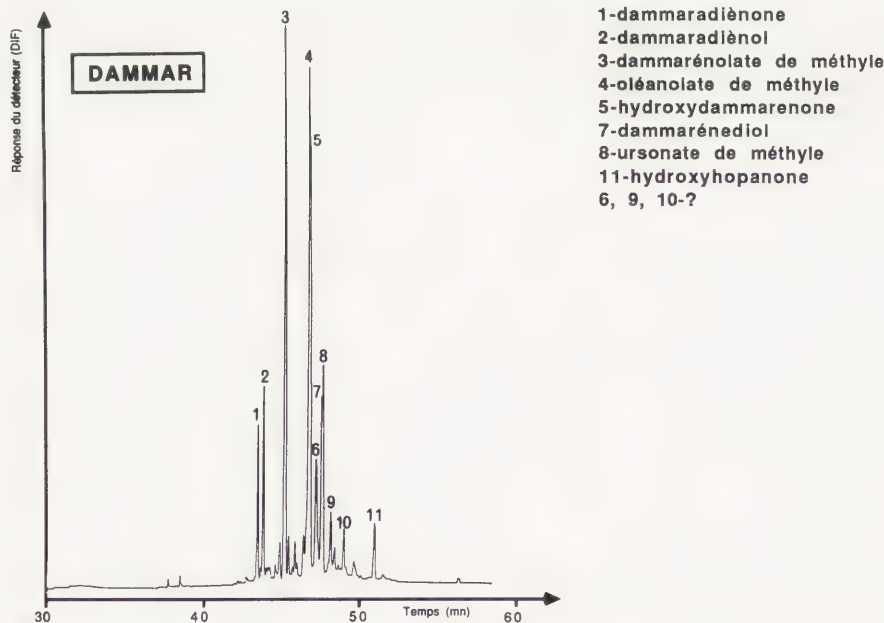
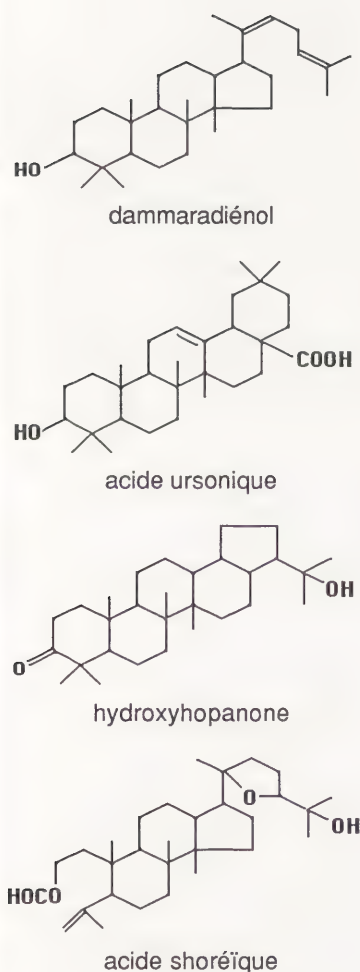


fig.3-chromatogramme de la fraction triterpénique de la résine dammar brute méthylée

FABRICATION ET ANALYSE DE PAPIERS TRANSPARENTS

Nous avons réalisé une modélisation sur du papier vélin et du papier vergé blancs, de grammage 80. Pour cela, on dépose à l'aide d'un pinceau plusieurs couches de chacune des solutions à appliquer. Les papiers obtenus ainsi qu'un témoin (non enduit) ont été vieillies dans un étuve sèche pendant plusieurs semaines. Ils sont alors finement découpés et extraits pendant vingt-quatre heures avec du chloroforme puis du méthanol. La fraction ainsi obtenue est analysée comme précédemment par CPG puis par CG/SM.

Le papier vélin a été enduit d'un mélange colophane/essence de térébenthine et exposé à 105°C pendant cinq et vingt-deux jours. Il a jauni et est devenu très cassant. Les pourcentages recueillis ont fortement diminué après les cinq premiers jours de vieillissement et semblent se stabiliser ensuite. En effet, l'extrait au chloroforme et au méthanol est passé de 25% pour le papier non vieilli à 17,5% pour celui vieilli 5 jours et à 16,3% pour celui vieilli 22 jours.

Dans l'extrait du papier non vieilli, sont présents les monoterpènes de l'essence de térébenthine (LONG, BUND,...), sauf l'a-PIN et le b-PIN éliminés pendant le séchage des papiers, et les acides terpéniques de la colophane. Cependant, on note une certaine dégradation de la colophane (disparition de PAL et NAB, diminution de ABT, apparition de DDA, DAB devient majoritaire) provoquée sans doute par l'extraction à reflux des deux solvants. Pour les papier vieillis, les acides ABT, PAL et NAB ont totalement disparu au profit d'une augmentation de DAB et DDA. Les quatre principaux produits de dégradation de la colophane apparaissent. Après vingt-deux jours, il y a autant de DDA que de DAB et l'OAB devient le pic majoritaire.

Avec le papier vergé, nous avons fabriqué trois types de papiers transparents: huilés, vernis et huilés/vernis (huiles de lin et de noix, pures ou diluées dans de l'essence de térébenthine; solution de colophane ou de sandaraque dans l'alcool,...). Dans tous les cas, l'extraction s'est avérée quantitative et nous avons montré que la prise d'essai pouvait être comprise entre 0,5 et 1 mg de papier. Comme précédemment, huiles et résines sont bien extraites des papiers et leur identification est facilitée en fragmentométrie. De plus, après vieillissement, les produits de dégradation obtenus sont bien ceux des résines ou des huiles pures vieilles artificiellement.

APPLICATION A DES CALQUES ANCIENS

Nous avons analysé les produits d'enduction de soixante-sept échantillons de papiers provenant de la bibliothèque de l'Ecole des Beaux-Arts de Paris (10 échantillons), du Maritime Museum de Londres (13 échantillons), du Musée du Creusot (18 échantillons), de la Société Panhard (11 échantillons), du National Park de Brooklyn (7 échantillons) et quelques divers prélèvements (7 échantillons), datés de 1800 à 1950.

Après extraction et analyse par CG/SM des produits d'enduction, nous avons rassemblé dans le tableau suivant les résultats :

BEAUX ARTS	MARITIME MUSEUM	CREUSOT	PANHARD	NATIONAL PARK	DIVERS
*D1	*MM101	°C3	*P3	°NP1	°FCB
*D2	*MM102	*C10	*P5	*NP2	*SAV
*DC	*MM104	°C11	*P11	°NP3	*CVD
*DF	**MM106	*C19	*P13	°NP4	°FCP
*64353	*MM107	°C20	*P14	*NP5	°FCV
*64386	°MM111	°C38	*P16	°NP6	*AD1875
*64370	*MM112	°C41	*P53	°NP7	*AD1918
*64385	*MM113	°C51	*P134		
*64344	*MM114	°C56	*P137		
*64359	*MM115	*C62	*P140		
	**MM116	°C64	*P144		
	*MM117	°C69			
	*MM120	°C71			
		°C73			
		°C76			
		°C87			
		°C91			
		°C98			
0 (°)	1 (°)	15 (°)	0 (°)	5 (°)	4 (°)
10 (*)	10 (*)	3 (*)	11 (*)	2 (*)	3 (*)
0 (**)	2 (**)	0 (**)	0 (**)	0 (**)	0 (**)

° = HUILE ; * = HUILE + COLOPHANE ; ** = HUILE + COLOPHANE + DAMMAR

Les dix papiers calques provenant de la bibliothèque de l'Ecole des Beaux-Arts de Paris datent de la période néoclassique (environ 1780 à 1825). Parmi eux, six proviennent de documents répertoriés (n°64344, 64353, 64359, 64370, 64385 et 64386) ; les quatre autres sont des échantillons dont nous n'avons pas pu définir le document d'origine. Les pourcentages d'extrait sont très importants et dépassent toujours les 40% et même 70% pour le calque n°64370. Les dix chromatogrammes sont similaires et montrent la présence de nombreux constituants lipidiques d'huiles (acides gras) et d'acides résiniques de la colophane (DAB, OAB,...etc). La seule différence existant se situe au niveau des proportions relatives des pics.

A titre d'exemple, nous donnons les chromatogrammes obtenus pour les extraits des calques n°64353 et n°64370 (Voir fig.4). Pour le premier, qui est très cassant et de couleur relativement foncée, on voit l'abondance du DIC9, OAB et la faible quantité d'ABT et de C18:1. Ceci est le reflet d'une dégradation importante de l'huile et de la résine. Au contraire, pour le calque n°64370, beaucoup plus clair et apparemment dans un état de dégradation moindre, un des pics principaux est le C18:1 ; l'OAB n'est plus le pic majoritaire et il reste encore une certaine quantité d'ABT. Ceci signifie que l'altération de l'extrait est moindre.

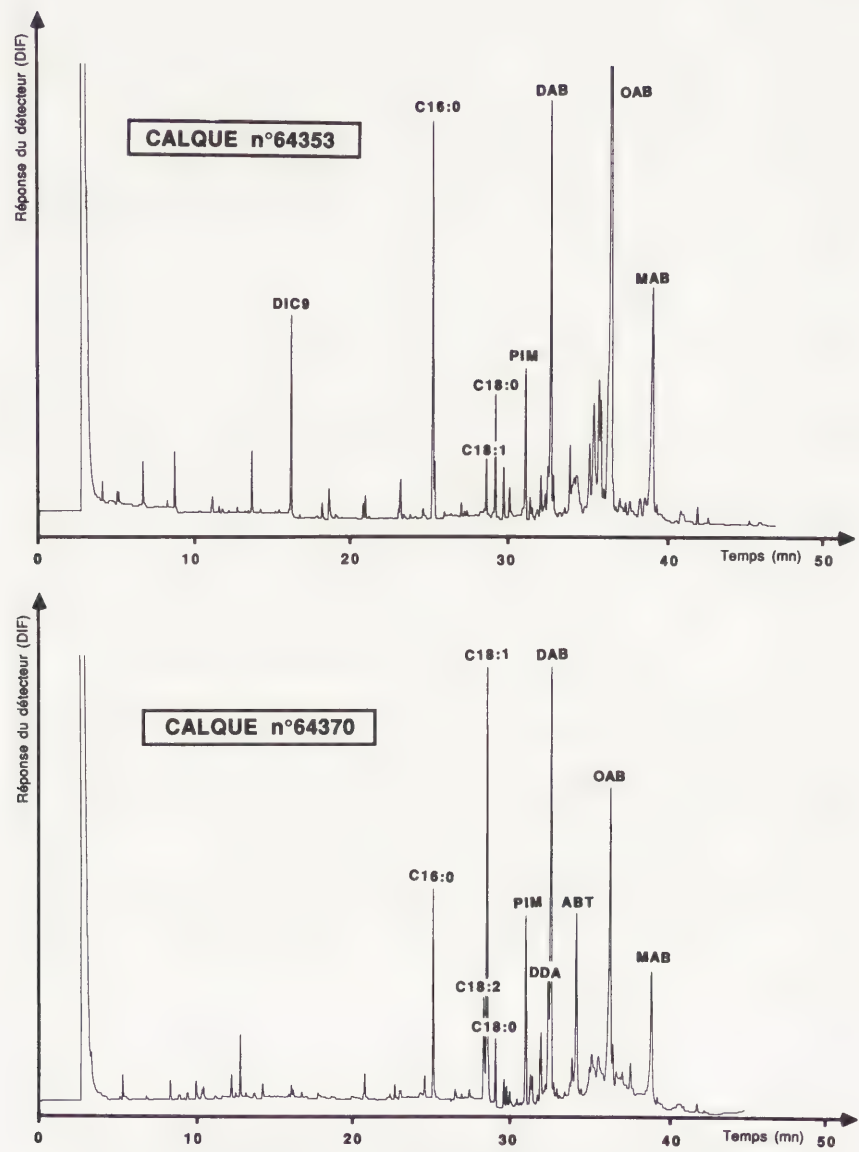


fig.4-chromatogrammes des extraits des calques 64353 et 64370
Les calques du Maritime Museum, du Musée du Creusot et de la Société Panhard sont plus récents (environ 1850 pour les premiers, 1866-1928 pour les seconds et début du siècle pour les derniers) et sont constitués également d'un mélange huile/résine (colophane). Deux calques du Maritime Museum (MM106 et MM116) sont enduits d'un mélange huile/colophane/dammar. En effet, un massif de faible intensité (Voir fig.5) élue en fin d'analyse, constitué de triterpènes de pic de base 143. Les papiers du National Park (1938-1950) sont enduits d'huile pour la plupart.

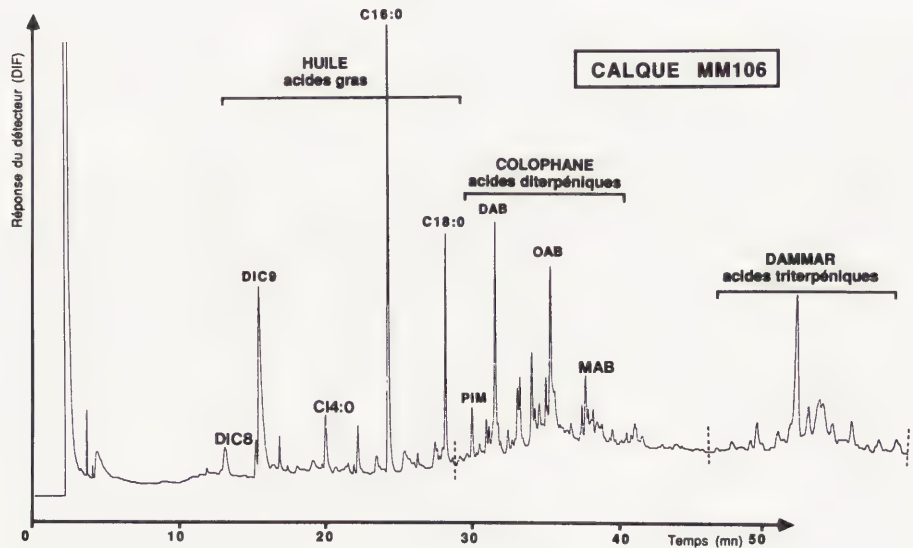


fig.5-chromatogramme de l'extrait du calque MM106.

On voit donc qu'il n'y a pas de règle générale pour le classement de ces papiers, quelles que soient l'origine et la date du document. La principale résine naturelle identifiée est de type **colophane**, mise en évidence par la présence de DAB et OAB. La nature exacte des **huiles** ne peut être déterminée avec précision. Nous avons, pour deux échantillons (Beaux Arts n° 64353 et Creusot : C10), réalisé deux analyses supplémentaires. La mise en évidence de triglycérides est la condition nécessaire pour confirmer la présence d'une huile. Pour cela, les triglycérides sont séparés de l'échantillon brut par chromatographie sur couche mince (CCM) sur une plaque de silice, avec comme éluant un mélange hexane/éther (9/1).

Après transestérification avec du BF₃/MeOH, ils sont analysés puis quantifiés par CPG. Dans les deux cas, les triglycérides représentent 30% en poids de l'extrait. De même, les acides gras totaux ont également été étudiés après saponification dans de la potasse alcoolique de l'extrait brut. Ils sont constitués d'acides gras saturés (C14:0 à C28:0), insaturés (C16:1w7, C18:1w7, C18:1w9 et C18:2) et ramifiés. Les acides résiniques de la colophane sont regroupés dans cette même fraction. Pour ces deux échantillons, la composition est donc un mélange huile/colophane (30/70).

CONCLUSION

Dans ce travail, nous avons montré que la composition des extraits des papiers transparents anciens permettait de bien définir les produits utilisés pour leur fabrication. La mise en évidence des produits de dégradation est facilitée par la recherche de certains ions caractéristiques de leur structure. Une modélisation, réalisée en fabriquant des papiers selon des procédés anciens, montre qu'il est possible d'extraire les produits d'enduction quantitativement et de les identifier sur des prélèvements inférieurs à 1 mg. Sur un échantillonnage de soixante-sept calques, de provenance et de date différentes, nous n'avons pas observé la grande diversité des matériaux décrite dans la littérature. Nous n'avons pu classer nos échantillons qu'en deux séries seulement : les papiers huilés et les papiers huilés / vernis. La seule résine présente est de type colophane sauf pour deux calques qui contiennent un mélange colophane/dammar.

BIBLIOGRAPHIE

- [1] F. Flieder, F. Leclerc, C. Laroque, P. Richardin, B. Guineau, "Analyse et restauration des papiers transparents anciens", in : Les Documents graphiques et photographiques. Analyse et conservation. Travaux du Centre de Recherches sur la Conservation des Documents Graphiques- 1986-1987, (Paris : La Documentation Française, 1988) : 107-116.
- [2] J.S. Mills, R. White, "Natural resins of art and archeology. Their sources, chemistry, and identification", Studies in Conservation 22 (1977) : 12-31.
- [3] J.S. Mills, R. White, The Organic Chemistry of Museum Objects (London : Butterworth and Co, 1987), 141-159.
- [4] Ibid, 83-110.
- [5] M. Derrick, "Fourier transform infrared spectral analysis of natural resins used in furniture finished", Journal of the American Institute for Conservation 28 (1989) : 43-56.
- [6] H.E. Audier, S. Bory, G. Defaye, M. Fetizon, G. Moreau, "Spectres de Masse de Terpènes : II - Influence du noyau aromatique sur la fragmentation des diterpènes tricycliques", Bulletin de la Société Chimique de France 10 (1966) : 3181-3186.
- [7] H.E. Audier, S. Bory, M. Fetizon, N.-T. Anh, "Spectres de Masse de Terpènes : III - Influence des liaisons éthyléniques sur la fragmentation des diterpènes", Bulletin de la Société Chimique de France 12 (1966) : 4002-4010.
- [8] T.-L.Chang, T.E. Mead, D.F. Zinkel, "Diterpene Resin Acids : Mass Spectra of Diterpene Resin Acid Methyl Esters", Journal of the American Oil Chemists' Society 48, n°9 (1971) : 455-461.
- [9] C.R. Enzell, R. Ryhage, "Mass Spectrometric Studies of Diterpenes : 1 - Carbodicyclic Diterpenes", Arkiv för Kemi 23 (1964) : 367-399.
- [10] Ibid, 26 (1966) : 425-434.
- [11] Ibid, 27 (1967) : 213-229.
- [12] C.R. Enzell, I. Wählberg, "Mass Spectrometric Studies of Diterpenes : 6 - Aromatic Diterpenes", Acta Chemica Scandinavica 23 (1969) : 871-891.
- [13] C.A. Genge, "Resins acids : Analysis by Mass Spectrometer (as Methyl esters)", Analytical Chemistry 31, n° 11 (1959) : 1750-1753.
- [14] D.F. Zinkel, L.C. Zank, M.F. Wesolowski, Diterpene resin acids. A compilation of infrared, mass, nuclear magnetic resonance, ultraviolet spectra and gas chromatographic retention data (of the methyl esters) (Madison : US Departement of Agriculture, Forest Service, Forest Products Laboratory, 1971), 1-191.
- [15] R. De La Rie, "Stable Varnishes for Old Master Paintings : Chemical composition of dammar resin" (Ph. D. diss., Université of Amsterdam, 1988) 45-66.
- [16] R. De La Rie, "Stabilized dammar picture varnish", Studies in Conservation 34 (1989) : 137-146.

ABSTRACT

In this study we have used samples of paper and parchment base from XIIIth to XVIth centuries, as well as different kind of metallogallic inks. The purpose of this paper was to establish the relationship between the degree of the darkness of the ink and its acidity, and also to evaluate the quantity of components in the reaction which produces metallogallic ink. Scanning electron microscopy and energy dispersive X-ray microanalysis were used to check ink penetration and component's distribution in the base of the document. Under identical analytical conditions, the presence of sulphur and iron was identified and its concentration was compared using X-ray spectra corresponding to the two elements, however, absolute measurement has not been carried out.

KEYWORDS

Paper, parchment, metallogallic ink, scanning electron microscopy, energy dispersive X-ray microanalysis.

SCANNING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE X-RAY MICROANALYSIS APPLIED TO METALLOGALIC INKS.

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Introduction

The purpose of this study is the identification of metallogallic ink components and their distribution on the surfaces to which they are applied. On conserved historical documents, we studied a great variety of manuscript inks with regard to their colour intensities and corrosion states. The variable components of light and dark inks on paper/parchment will also be described.

Metallogallic inks are prepared from various combinations of tannin, iron sulphate, and copper sulphate. We studied how these components react in relation to the supposed characteristics for each kind of ink. All the ink recipes available to us listed organic components from vegetal extracts: galls, fruits and bush leaves, barks and trees' medulla (1). The vegetal tannins are usually complicated mixtures containing hydrolysed and condensed tannins; those used to prepare the inks are normally the gallotannins. A reaction between gallotannins and iron sulphate yields ferrogallic ink: the interaction between Fe ions and the organic compounds give a coloured compound that is called ink. The oxidation reaction of Fe^{2+} to Fe^{3+} forms a complex with gallotannin hydroxyl groups, yielding a colloidal precipitate in suspension.

The visual comparison of different inks on historic documents offers a clue that light inks lack organic components; however, tannin was detected in dark inks. Gallic acid is present in some samples, although the quantity diminishes in inks of advanced antiquity (2). The lack of gallic acid can be attributed to oxidation (which would change the compound into other degradation products), or to an originally small quantity of complex present at the time of ink application.

The interaction between Fe ions and gallic acid forms a complex by coordination, resulting in a structure similar to quinone or its analogs (See fig.1).

Coordination with iron is feasible with more than one gallic molecule; probably the colour intensity increases with the coordination of the complex. However, the organic molecule can change over the time, and could almost disappear if originally is present in only a small quantity, whereas the iron remains in oxide form.

Many ancient documents from the thirteenth to fifteenth centuries have light ink; some documents from the fifteenth century also have darker colour scripts. Either the inks contain enough tannin to retain the darker coloration, or the presence of sulphuric acid causes an incipient carbonization of the paper ground.

The ink preparation behaviour will be discussed in terms of data obtained from light microscopy, scanning electron microscopy, and energy dispersive X-ray microanalysis. Samples were taken of light, oxide coloured, dark inks applied to paper and parchment. Very acidic ink samples were also examined (3).

Light Microscopy.

The corrosion of acidic inks on paper and parchment can be seen by visual examination. The ink penetration and distribution on these base textures yields such basic information as colour intensity or total alteration of the fibres.

The parchment surface is easily distinguishable from the ink. Penetration of inks into the paper or parchment is less marked for light than dark - coloured inks. Typically, the penetration of an ink is deeper on paper than on parchment. The parchment structure does not allow for the easy migration for iron, which is restricted to the surface.

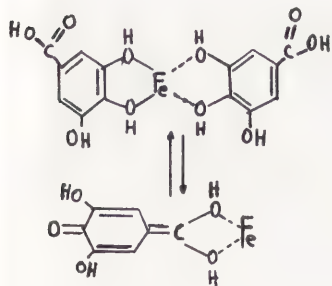


Fig. 1
Ferrogallic complex

Very acidic inks retain a dark black colour, and corrode the surfaces to which they are applied; this activity can extend throughout the entire paper surface, as can be seen in cross-sections of paper or parchment.

Scanning electron microscopy

Because paper and parchment are composed of fibres, simple cuts with a bistoury result in topographical irregularities which interfere in the proper visualization of cross-sections; congelation fractures were unsuccessful also. The best samples were obtained from cross-sections of resin-imbedded fragments.

The samples were prepared as follows. After exposure to a vacuum to eliminate inherent moisture, the paper/parchment fragments were imbedded in SPURR resin (4) and prepared for scanning electron microscopy (SEM).

A back-scattered electron image allows a recognition (by the grey level) of the heavier elements on an organic base (See figs. 2-5). Once the location and depth of penetration of the ink is determined, specific areas were analyzed by energy dispersive X-ray microanalysis (EDX) for the presence of Fe, S, Ca, Cu and other elements (5),(6).

The EDX spectra of analyzed samples offer qualitative information on elemental composition, distribution, as well as ink penetration. Although not absolutely quantitative, this technique enables a comparison between similar samples. Conclusions can also be drawn about ink compositions and its behaviour. The relative quantities of S and Fe in specific areas of ink, for instance, may relate to its acidic components. If Cu is detected in the sample, the contribution of copper sulphate in the ink formula can be confirmed. If the Fe/Cu ratio is high, the copper source is considered to be an impurity of the iron sulphate.

This microanalytical technique makes it possible to record a map the distribution of Fe in the base thickness. In some cases it is useful to corroborate its presence and iron's superficiality.

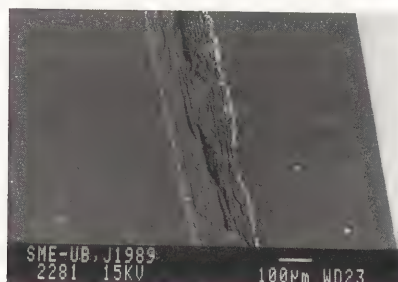


Fig. 2. SEM picture, back scattered image. Parchment base. Light ink. (7).

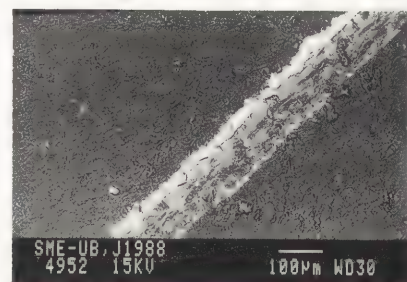


Fig.3. SEM picture, back scattered image. Parchment base. Black ink. (8).

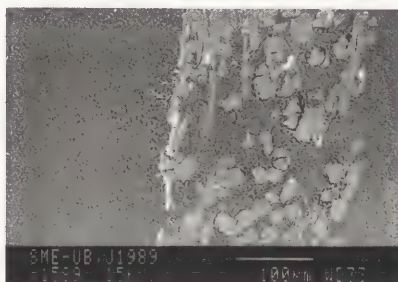


Fig.4. SEM picture, back scattered image. Paper base. Light ink. (9).

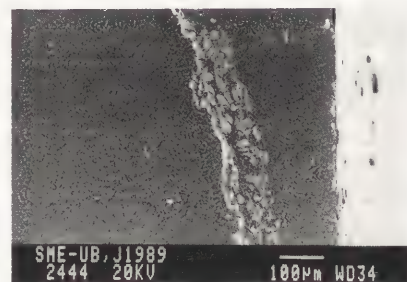


Fig.5. SEM picture, back scattered image. Paper base. Black ink. (10).

Ink behaviour on paper and parchment.

Let's begin with the basic reaction of inks, and then discuss the factors that intervene and determine its behaviour.



In ancient ink recipes we find iron sulphate and tannins extracted from vegetables (gallnut, sumac, etc.) The extraction of these substances is a complex and time-consuming process. Texts with ink recipes often recommend taking advantage of what remains of one ink to prepare another. There probably are a few concentration of tannins in the vegetable extracts of water or alcohol.

The iron sulphate could be contaminated by some impurities, such as copper sulphate. As it is a solid, it is easy to grind, weigh and manipulate.

The iron sulphate and galls extract mixture has a high proportion of sulphate to assure the formation of ink. The quantity of tannins in gall extract depends on gall quality and the extraction time. It is possible that the ancient preparation of metallogallic inks from vegetable extracts was made with an excess of iron sulphate. If this hypothesis is true, a theory about ink characteristics as related to component proportions can be formed. Microanalytical data and electron micrograph images can corroborate that theory.

We analysed light-coloured ink samples from documents dating from the fourteenth and fifteenth centuries. (See figs. 6,7). The paper base was in perfect condition, and no clear signs of degradation on the sample were visible. Probably a non-acidic ink made with an excess of iron sulphate was used.

We suppose initial ink reaction yields ferrogallic complex in suspension, sulphuric acid and ionized iron sulphate (Fe^{2+} , SO_4^{2-}) (11). From the established conditions of inks with an excess of iron sulphate, we can propose a different behaviour for each compound. The ferrogallic complex has a relatively low penetration capacity because it is a particle. The sulphate ions can be easily introduced into the structure of paper, but the Fe ion is held by the hydroxyl groups of cellulose. We define the behaviour of these components and their locations on the paper as follows:

First: The iron will be always placed in superficially on the base, whether the source is the complex suspension or an iron sulphate excess.

Second: The presence of sulphur can be attributed to sulphuric acid, which is a by-product of the interaction of tannin and ferrous sulphate. The acid will quickly react with the paper's calcium carbonate to form calcium sulphate. We know through experience that a light ink is not very acidic.

Third: The sulphate ion which comes from the iron sulphate excess will easily penetrate the paper in large quantities.

Fourth: The Fe ion, which comes from the iron sulphate excess, can precipitate (See figs. 8,9). Both diagrams show the conditions under which the hydroxyl will precipitate, and also the different compounds, and their concentration, that can be present in the dissolution related to the pH. Over time the hydroxyl becomes basic oxides which are more stable and are responsible for light coloured ink.

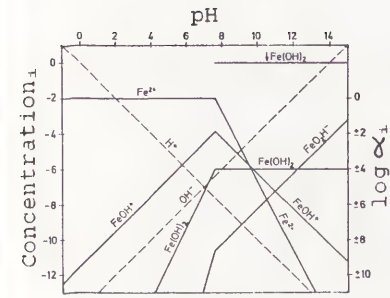


Fig.8 Logarithmical diagram. Fe (II)-OH system. C= 10⁻²M.

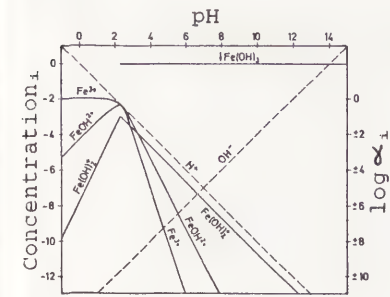


Fig.9 Logarithmical diagram. Fe (III)-OH C = 10⁻²M.

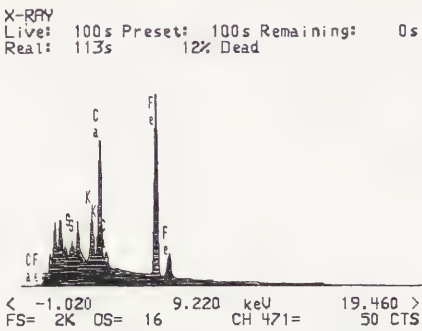


Fig. 6. Spectrum of a paper sample of a light ink in a specific area with ink.

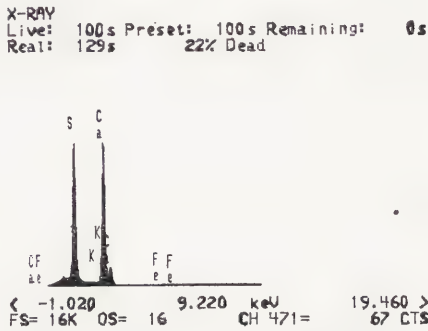


Fig.7. Spectrum of the same paper sample with light ink in a specific area without ink.

Similarly, in documents with considerably more acidic ink, large quantities of organic compounds (tannin, gallic acid) influence the production of more sulphuric acid, because more iron (II) sulphate can react in the presence of sufficient tannic compounds. The colouring will be darker for the complex, due to increased coordination. The inks will also be more corrosive.

The sulphur content of some areas of ink will be considerably higher due to the immediate reaction of sulphuric acid with calcium carbonate. If not enough carbonate is present to interact with the sulphuric acid, it penetrates the paper and causes its dehydration. Therefore, the presence of corrosive black inks is evidence of various degrees of carbonization, depending on the amount of sulphuric acid in the ink.

The analysis of a unembedded sample with acidic ink showed higher values of S than Fe. Excess of S, probably caused by sulphuric acid, was found on the surface and inside the paper.

A parchment sample with a superficial layer of relatively unacidic dark ink had a much higher S/Fe ratio than a light ink sample. (See Figs. 10,11). We attribute the presence of sulphur, in a specific area with ink, to sulphuric acid, as in the case noted above.

Dark inks are the result of higher tannin content. The colouration is deeper, but it was difficult to obtain the right proportion between iron (II) sulphate and tannins to achieve a dark but relatively non-acidic ink. When the quantity of sulphuric acid is too high, its reaction with the paper or parchment base will cause carbonization.

When dark ink is removed from the parchment, a light colouration of iron oxide remains. Part of the iron remains in the fibres and later becomes oxide, but all this phenomenon happens under a coat of dark ink. There is no doubt that the hydrolysis of gallotannins yields sugar and gallic acid; the carbonization of the sugar will colour the ink too. Although this colouration is due to sulphuric acid originally present in the ink, it is clear that this carbonization occurs when the ink is sufficiently acidic. There might also be some residue of gallic acid, which helps retain the dark colour.

We analyzed a greenish ink found some documents from the "Archivo de la Corona de Aragón". (See fig. 12). We used the same preparation and technique of analysis that we had used for the other samples. The EDX spectrum confirmed the presence of equal amounts of iron and copper. The greenish colouration is due to the green copper hydroxycarbonates. In addition to the brownish tonality from the iron oxide, this explains the special ink's colouration.

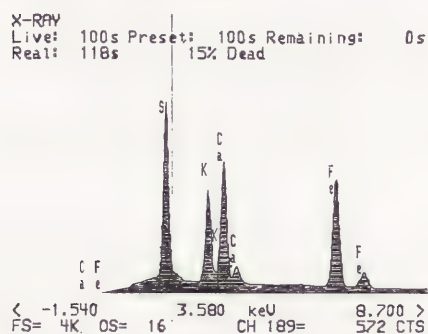


Fig. 10. Spectrum of a parchment sample of a dark ink in a specific area with ink.

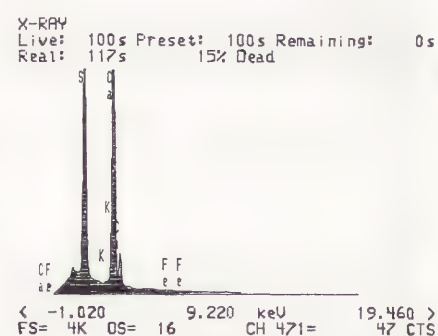


Fig. 11. Spectrum of the same parchment sample of a dark ink in a specific area without ink.

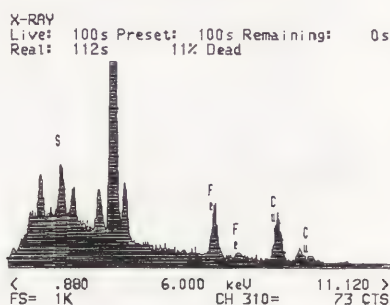


Fig. 12 Spectrum of a paper sample of a greenish ink in a specific area with ink.

Conclusion.

Both scanning electron microscopy and energy dispersive X-ray microanalysis are valuable techniques to investigate metallogallic manuscript ink composition and penetration. Determining the elemental composition and the locations of certain elements in the compound under certain conditions allows an interpretation of their behaviour.

Ink prepared with an excess of iron sulphate explains the presence of iron oxides, which colour the non-acidic inks.

The gradual colouring increase is related to large quantity of tannins. An increase of sulphuric acid can be deduced if the spectrum shows higher sulphur in the ink.

An excess of sulphur, related to sulphuric acid, provokes a carbonization process, which results in dark inks. The scarcity of sulphur in a specific area of light ink is related to sulphuric acid content, if the sulphuric acid is in a dark ink, it could also affect the rest of the base.

NOTES.

1. The tannins are divided in hydrolysed, like the gallotannins and the ellagitannins, and condensed, which treated with acids, they become complex substances. When the gallotannins hydrolyse, as a result they give sugar and gallic acid. In a similar process, the ellagitannins bring sugar and ellagic acid.

2. Arpino, P. and Moreau, J.P., Oruezabal, C. and Flieder, F. "Gas Chromatographic-Mass Spectrometric analysis of tannin hydrolysates from the ink of Ancient Manuscripts. (Xth. to XVth. century)". Journal of Chromatography, 134 (1977), 433-439.

3. The documentation here used comes from the "Archivo de la Corona de Aragón". They are some late medieval and XVth century passages with no special value.

4. 10 gr. ERL C₈ H₁₂ O₈ 4 Vinylcyclohexene dioxide. FLUKA 94956; 6 gr. DER. 736. Epoxy-resin FLUKA 31191; 26 gr. NSA C₁₃ H₂₀ O₃ . 2 Nonen-1-ylsuccinic anhydride. FLUKA 74378; 0.4 gr. S-1.2 Dimethylaminoethanol. FLUKA 38990. To avoid resin's fragility, we add 0.8 gr. Dibutyl phthalate. FLUKA 44610, 44614.

5. Conditions in microanalysis: Beam current, 0.8 10⁻⁹ A.; accelerating voltage, 20 kV; 100.000 magnification; working distance 33 mm. Used model JSM 840 (Jeol Ltd.) with scanner AN 10000 (LINK SYSTEMS) with Be window.

6. This essay has been possible thanks to a contract between the Spanish Ministry of Culture and the Electron Microscopy Service from Barcelona University. I want to thank all the staff of this Service and especially Jordi Blavia and Ramon Fontarnau.

7. Working conditions. Beam current: 0.6 10⁻⁹ A.; accelerating voltage: 15 kV; working distance: 23 mm.; magnification: 95.

8. Working conditions. Beam current: 0.6 10⁻⁹ A.; accelerating voltage: 15 kV; working distance: 30 mm.; magnification: 130.

9. Working conditions. Beam current: 0.6 10⁻⁹ A.; accelerating voltage: 15 kV; working distance: 33 mm.; magnification: 230.

10. Working conditions. Beam current: 0.8 10⁻⁹ A.; accelerating voltage: 20 kV; working distance: 33 mm.; magnification: 130.

11. Experience shows that dissolutions of Fe (II), become quickly oxidized at the air with Fe (III).

B I B L I O G R A P H Y

Allinger, Química Orgánica. (Barcelona. Reverté. 1974.)

A. Altisent, "Persistència als segles XVIII i XIX de la fórmula medieval de la tinta" Estudis d'història medieval. I (1969), 137-139.

P. Arpino, J.P. Moreau, C. Oruezabal, F. Flieder, "Gas chromatographic. Mass spectrometric analysis of tannin hydrolysates from the ink of ancient manuscripts (Xth to XVth century)". Journal of Chromatography 134 (1977), 433-439.

G. Banik, H. Stachelberger, K. Messner, "Untersuchungen der destruktiven Wirkung von Tinten auf Schriftträgermaterialien." Restauro. (1988, 4), 302-308.

W.J. Barrow, Manuscripts and documents. their deterioration and restoration. (Charlottesville. 1972.)

Becker Wentworth, Química General. (Barcelona. Reverté. 1984.)

M.Darbour, S.Bonnassies, F.Flieder, "Les encres metallo-galliques étude de la degradation de l'acide gallique et analyse du complexe ferrogallique." Comité pour la Conservation. ICOM. 6ème reunion triennale. (Ottawa. 1981.) 81/14/3.

I.L. Finar, Química Orgánica. vol.II.(Barcelona. Alhambra.1966.)

F.Flieder, C.Oruezabal, R.Barroso, "Analyse des tannins hydrolysables susceptibles d'entrer dans la composition des encres ferrogalliques." Comité pour la Conservation. ICOM. (Venise. 1975.) 75/15/12.

F. Flieder, La conservation des documents graphiques. Recherches expérimentales. (Paris. Eyrolles. 1969).

F. Margival, Les encres usuelles. (Paris.Desforges-Giradot.1928.)

M. de Pas, "La composition des encres noires." Les techniques de Laboratoire dans l'étude des manuscrits. Colloques Ints. CNRS. 548 (1974), 119-132.

M. de Pas, "Etat des travaux effectués sur l'analyse des constituants des encres noires manuscrites par deux techniques:chromatographie sur couche mince et electrophorèse." Comité pour la Conservation. ICOM. (Venise. 1975.) 75/15/9.

M. de Pas, "Recherches sur les encres noires manuscrites." La Paleographie grecque et byzantine. Colloques Ints. CNRS, 559, (Paris. 1977), 55-60.

P. Riberau-Gayon, Les composés phénoliques des végétaux. (Paris. Dunod. 1968.)

M.C. Sistach, "Aportación al estudio de la composición química de las tintas. Algunos ejemplos catalanes." VI Congreso de Conservación de Bienes Culturales. Tarragona 1986. (Barcelona. 1988), 302-309.

R.Talbot, F.Leclerc, F.Flieder, "Etude de la régénération chimique des encres metallo-galliques." Comité pour la conservation ICOM. (Zagreb. 1978.) 78/14/9.

R. Talbot, F. Leclerc, F. Flieder, "La détérioration des encres metallo-galliques et leur régénération chimique." Les documents graphiques et photographiques. Analyse et conservation. CNRS. (Paris. 1981), 41-70.

T. Torio de la Riva, Arte de escribir por reglas y con muestras. (Madrid. 1798.)

J. Trenchs, M. Cárcel, "La tinta y su composición. Cuatro recetas valencianas. (s.XV-XVII)". Rev. Archivos,Bibliotecas y Museos, LXXXII (1979), pp. 415-426.

B.Y. Zerdoun, Les encres noires au Moyen Age (jusqu'a 1600). (Paris. CNRS. 1983.)

ABSTRACT

In 1957, the parchment of the "Codex Eyckensis" (eighth century AD) was systematically laminated with the commercial plastic film "Mipofolie". This material was found to be an externally plastified polyvinylchloride. According to its composition, the following ageing effects could be put forward: formation of hydrochloric acid that may acidify the parchment, yellowing of the plastic that influences the legibility of the text and the appearance of the illustrations, migration of the monomeric plasticizer that causes enhanced transparency and colour changes of the parchment, possible co-migration of polymer solubilized in its plasticizer into the porous parchment structure, enhanced brittleness of the sandwich. Mipofolie was removed with amylacetate/ethanol (1/4), applied with a brush to the contact zone between parchment and plastic. Illuminated sheets were put in a bath and the PVC on areas where pigments were applied with high relief onto the parchment was pricked to locally speed up the effect of the solvent. Any visual disruption of the parchment structure was repaired by treatment with a slightly moistened cotton.

KEY WORDS

Parchment, codex, lamination, Mipofolie, polyvinylchloride, conservation, delamination

THE CODEx EYCKENSIS, AN ILLUMINATED MANUSCRIPT ON PARCHMENT FROM THE 8TH CENTURY AD. LABORATORY INVESTIGATION AND REMOVAL OF A 30 YEAR OLD PVC LAMINATION

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Introduction

The Codex Eyckensis is an illuminated manuscript on parchment from the 8th century AD, that actually belongs to the treasury of the Saint-Catherine's church at Maaseik (province of Limburg, Belgium). It formerly belonged to the Benedictine convent of Aldeneik, situated 3 kilometers to the North-East of Maaseik. Together with other properties of the convent, the Codex Eyckensis was transferred to Maaseik in 1571. Since then, it resides in the cited church. The codex consists of 133 sheets with maximum dimensions of 18 x 24 cm (see fig. 1). Before conservation, it was thoroughly investigated for its textual and codicological characteristics (1).

In 1957, the sheets of the manuscript were packed in plastic material, "Mipofolie", many of them over their entire surface and even on both sides. In January 1986 our institute was asked by the "Bestuur voor Monumenten- en Landschapszorg" (Committee for the Care of Monuments and Landscapes) to investigate the actual condition of the Codex Eyckensis and to propose methods and products for its conservation. In a first phase, the chemical nature of Mipofolie was investigated and the plastic was removed from the parchment. In a second phase will be investigated materials and methods that should be used in a future conservation and, finally, in a third phase this new conservation will be executed. The activities of the second and the third phase will be reported in papers to follow.



FIGURE 1: Canon tables from the Codex Eyckensis; left: folio 2 recto, right: folio 11 verso.

The chemical composition and application of Mipofolie

Mipofolie was a product of "Alfred Schwarz GmbH & Co", Overath-Untereschbach, GFR. A letter wherein more information was asked regarding the composition, fabrication and way of application of this material, was never answered.

A piece of plastic was removed from the parchment with a scalpel and was analyzed by infrared spectrometry (FTIR, Nicolet 5DXC). From the individual interpretation of the peaks and from a matching procedure of the entire spectrum to a library of polymers, it was concluded that Mipofolie was an externally plastified polyvinylchloride (PVC). The IR spectrum of the whole film is given in figure 2a; that of a pure PVC from the library in figure 2b.

The amount of monomeric plasticizer was calculated after extraction of a preweighed sample of Mipofolie in ether, at the boil for 7 hours (2). Two separate determinations gave 30.7 and 30.3 % by weight, respectively. The chemical nature of the monomeric plasticizer was determined by NMR spectroscopy and gas chromatography to be bis(2-ethylhexyl)phtalate, commonly called dioctylphtalate, that is one of the commonly used monomeric plasticizers for PVC (3). Polymeric plasticizers were removed with methylalcohol (at the boil, 8 hours, 2 consecutive extractions). The polymeric residue was solubilized in tetrahydrofuran and precipitated by the addition of ethylalcohol. The precipitate was washed with ethylalcohol and dried (2). The IR spectrum of the residual polymer is presented in figure 2c.

FIGURE 2a: FTIR of Mipofolie sheet.

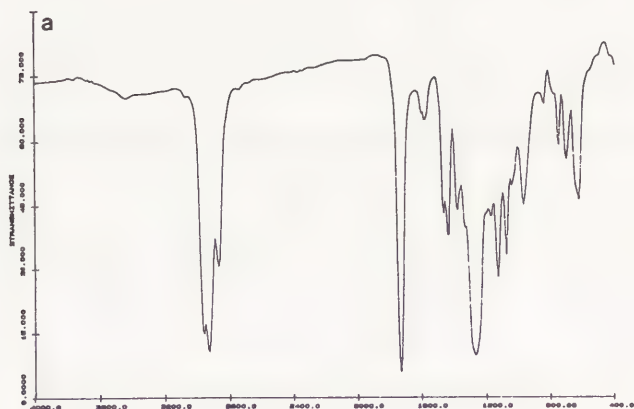


FIGURE 2b: FTIR of pure PVC from library.

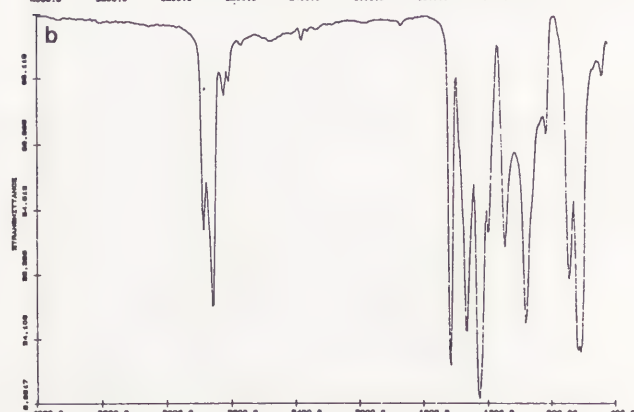
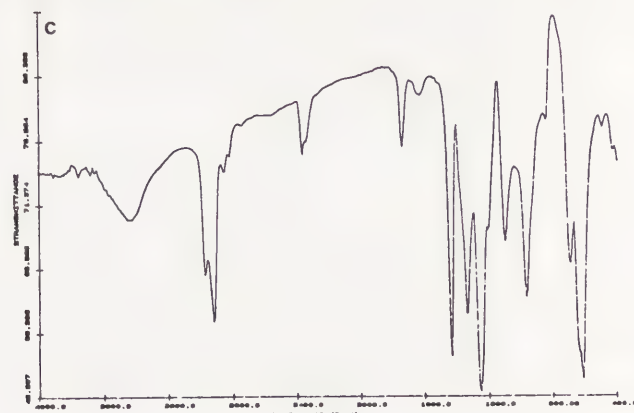


FIGURE 2c: FTIR of Mipofolie polymer.



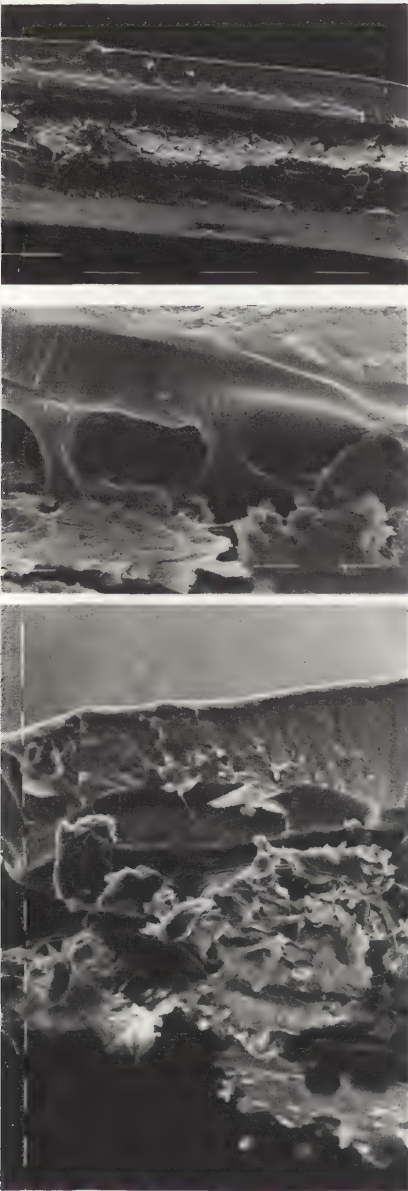


FIGURE 3: scanning electron microscopy of the sandwich Mipofol.-parchment-Mipofol. Upper: complete sandwich, 160x magn.; middle: detail from upper, 1250x; lower: close contact between Mipofolie and parchment, 640x.

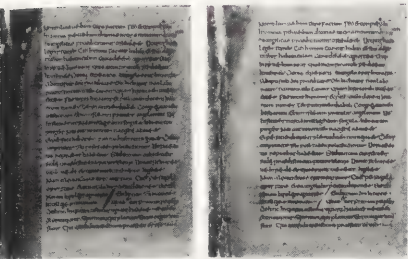


FIGURE 4: yellowing (darkening) effect of aged Mipofolie on underlying parchment; Codex Eyckensis folio 59 recto; left: before removal of Mipofolie; right: after removal.

There was found no indication for polyvinylacetate (PVA) to be present as a copolymer for plastifying purposes or for raising the polymer's adhesion properties of the contact-making surface of the sheets. This would however be indicative for the way in which the sheets were applied to the parchment: by "glueing" under moderate pressure (hand, press) or by heat-sealing. In this context, literature data are not unambiguously clear either: Werner mentioned the presence of a glueing layer that made possible the lamination with Mipofolie at room temperature and at moderate pressure; in the same article is stated that since 1954, PVC sheets are used at the "Istituto di Patologia del Libro" (Rome, Italy) to laminate parchment by heat-sealing (4). Wächter describes the delamination of a Carolingian evangelarium from the eighth century and he clearly refers to a glueing layer that remains visible on the parchment's surface after removal of the Mipofolie in the solvent butylacetate/amyacetate/ethanol (1/1/4) (5). However, no chemical analyses were executed, neither on the whole sheets nor on the remaining layer.

In figure 3 is presented a series of photographs of a cross-section of the sandwich Mipofolie-parchment-Mipofolie taken with a scanning electron microscope (SEM). In figure 3a is seen the complete sandwich's cross-section. There is a remarkable difference in the way the Mipofolie adheres to the parchment. On top, the contact is not very close and adhesion is provoked by the formation of amorphous bridge-like structures. At the bottom, there is a very close contact between Mipofolie and parchment so that practically no voids are left between the two layers. The thickness of Mipofolie is about 80 μ m. In figure 3b is given a detail of the bridge-like structures that provoke adhesion of Mipofolie on parchment. It is clear that the plastic is introduced as an amorphous molten mass in between the collagen fibres of the parchment. Figure 3c shows an enlarged picture of a "close contact" zone where the introduction of amorphous mass into the fibrous parchment structure can also be seen. In no picture is evidenced any discontinuity in the cross-sectional view of Mipofolie.

Ageing effects of Mipofolie

According to its chemical composition, several ageing effects of Mipofolie and, indirectly, on the laminated parchment may be put forward.

First of all, the generation of hydrochloric acid (HCl) is propagated by heat and light, causing the decomposition of the polymer chain by an un-zipping mechanism (3). At the same time, double bonds are formed which, when conjugated in a series of five or more, may cause yellowing. Hydrochloric acid may acidify the parchment and the yellowing may alter the appearance of the illustrations and the text. The pH of the parchment was measured both on a surface never covered with Mipofolie and on a covered place. With the aid of a capillary, a microspot was put on the surface and the colour developed was interpreted with the aid of a binocular (indicator 1: bromocresolgreen; indicator 2: bromocresolpurple); similar hues were obtained for both areas, suggesting a comparable pH between 5 and 6.5. For the time being, obviously no measurable acidifying action was imposed by Mipofolie on the parchment. However, yellowing of Mipofolie was clearly noticed, so that the inherent formation of hydrochloric acid may be expected to become effective in the future.

The plastifier present in Mipofolie is a liquid. Despite a boiling point of over 300°C, it will gradually evaporate and it may also migrate into neighbouring materials. Those effects will cause hardening of the PVC film and enhanced transparency and/or discoloration of the parchment. This enhanced transparency, although clearly visible with the naked eye, is difficult to illustrate in a photograph, but darkening of the sandwich clearly is (see fig. 4). The plasticizer is also a good solvent for the polymer it plastifies, so that co-migration of PVC into the fibre structure of the parchment may occur. This would result in a deposition of PVC on the collagen fibres.

According to all these data it was decided to remove the PVC sheets from the parchment.

Removal of Mipofolie

Preliminary attempts to remove the PVC from the parchment were made without the use of any solvent or swelling agent. However, not many occasions were encountered where Mipofolie could be removed in a pure mechanical way without seriously damaging the surface of the parchment and without any danger for the text and some pigments. Slight warming with an infrared lamp improved the mechanical removal when working between 35 and 40°C, but then an important amount of PVC remained on the parchment.

The first attempts to remove Mipofolie with the aid of organic solvents were performed at the "Institut für Restaurierung, Oesterreichische Nationalbibliothek, Wien", under the supervision of Prof. O. Wächter and Dr. G. Banik. One sheet with only text and an illuminated one, that were both completely covered at both surfaces, were liberated from Mipofolie in a bath of amylacetate/ethanol (1/4) according to the method outlined previously (5). Few difficulties were encountered with the written sheet, but on the illustrated one appreciable amounts of plastic remained on the surface; and these could not be completely removed, not even with pure amylacetate. Also some parts of a red pigmentation, that is present on the parchment with high relief, were removed together with the swollen plastic. Since it was not unlikely that any swollen (partially solubilized) PVC could be entrapped in the fibrous structure of the parchment, a cross-section of delaminated parchment was looked at with SEM (see fig. 5). In the interior of the sheet, some amorphous and fibre-adhering bridge-like structures were found that could be compared to those found in the contact zone between Mipofolie and parchment (see fig. 3a-c). It must be emphasized however that this picture was the only one to be found in the whole sample and that this kind of deposition could also have been caused by co-migration of PVC solubilized in its own plastifier (see: ageing effects of Mipofolie) previous to the delamination. Nevertheless, it was decided to limit the danger for internal migration of PVC by restricting the bathing procedure as much as possible.



FIGURE 5: SEM of a cross-section of parchment, delaminated in a bath of amylacetate/ethanol (1/4, v/v).

The final method adapted was as follows. Mipofolie was mechanically removed at an edge of a sheet over a few millimeters only. Then, with a soft brush a small amount of solvent (amylacetate/ethanol, 1/4) was applied to the contact zone and the Mipofolie could be pulled away with a force that was considerably smaller than without the use of a solvent. If plastic material was seen to remain on the parchment, then these zones were carefully rubbed once and in one direction with tissue paper, when the solvent was nearly evaporated.

On some occasions the surface structure of the parchment was disrupted, resulting in a striped pattern. Treatment of the disrupted surface with a slightly moistened cotton let recombine the disturbed fibres to a normal plain structure.

To remove Mipofolie from the illuminated sheets, it was necessary to use the bathing method and even then some red pigmentation was lost if no precautions were taken. Therefore, the PVC was pricked around red pigmented zones to let introduce the solvent more quickly there. Gradually, the small holes were used to lift the plastic with a wooden spatula and so, the Mipofolie could be removed from the red pigmented zones almost without any loss of the pigment.

Conclusion

The plastic material "Mipofolie" was identified as a vinylchloride polymer, externally plasticized with 30% (w/w) of bis(2-ethylhexyl)phtalate. In 1957 it was systematically applied to the parchment of a codex from the 8th century AD by heat-sealing.

The chemical nature of the polymer let us decide to remove the Mipofolie from the parchment. This was achieved with a swelling solvent (amylacetate/ethanol, 1/4, v/v), either applied with a brush to the contact zone between plastic and parchment, or used as a bath wherein the laminated parchment was immersed. This latter method must be used on illuminated sheets to prevent the loss of pigments that were applied to the parchment with considerable relief. All Mipofolie removed is kept in paper portfolios and will make part of the final report to be made at the end of the conservation. It is possible that bathing causes migration of swollen PVC into the parchment, but it was decided

that this phenomenon was no reason for not undoing the lamination. Nevertheless, whenever possible, the bathing method was avoided.

It was noted that removal of the plastic enhanced the contrast between text and illustrations on one hand and the parchment background on the other. Also the transparency of completely laminated sheets diminished considerably. Any disruption of the parchment surface, caused by the mechanical removal of Mipofolie, was corrected by slight local humidification.

Acknowledgement

The authors are greatly indebted to Prof. O. Wächter and Dr. G. Banik for the execution of some experiments at the Restoration Institute of the Oesterreichische Nationalbibliothek in Vienna. We also thank Mr. Cillis from the "Koninklijk Belgisch Instituut voor Natuurwetenschappen" for taking and interpreting the SEM pictures.

References

1. A. Derolez, "Codicologisch en tekstueel onderzoek van het Evangelarium van Maaseik (8ste eeuw)" (Internal report K.I.K., October 1989), 36pp.
2. J. Haslam and H.A. Willis, Identification and analysis of plastics (London: Iliffe books Ltd., 1965), 47-50.
3. W.J. Roff and J.R. Scott, Fibres, films, plastics and rubbers (London: Butterworths, 1971), 110-111.
4. A.E. Werner, "The lamination of documents" (Report presented to the Joint Meeting of ICOM Committee for museum laboratories and ICOM sub-Committee for the care of paintings, Washington and New York, September 17 - October 1, 1965) 10pp.
5. O. Wächter, "Die De-Laminierung des karolingischen Evangeliums aus dem Essener Domschatz," Maltechnik-Restauro 93,2(1987)34-38.

RESUME

On a essayé de faire simultanément un traitement désacidifiant et fongistatique avec du propionate de calcium, un composé non toxique connu déjà comme inhibiteur du développement des microorganismes.

On a effectué des essais concernant le degré de blancheur, le pH, le degré de polymérisation et les spectres IR sur des échantillons de papier Whatman témoin et oxydé avec de l'hypochlorite, traité et non traité avec du propionate, avant et après un vieillissement accéléré à 80°C et à une HR de 76%.

A l'issue de cette première recherche, le propionate de calcium se révèle un bon agent désacidifiant et stabilisant de la cellulose, en particulier si celle-ci est traitée avec de l'hypochlorite de sodium.

MOTS CLEFS

Propionate de calcium, désacidification, oxydation, hypochlorite de sodium, spectres IR, cellulose, dégradation, stabilisation.

LE PROPIONATE DE CALCIUM: AGENT DESACIDIFIANT ET STABILISANT DES PAPIERS ANCIENS?

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Introduction

Le but de la recherche expérimentale que l'on décrit dans cet article a été d'évaluer l'efficacité du propionate de calcium en tant qu'agent désacidifiant pour les documents sur papier acide et de vérifier d'autres effets éventuels, positifs ou négatifs, pour leur conservation.

Le propionate de calcium, $\text{Ca}(\text{CH}_2\text{CHCOO})_2$, est une poudre blanche très soluble dans l'eau (40 g dans 100 cc à 0°C et 56 g dans 100 cc à 100°C), peu soluble dans l'alcool éthylique et méthylique et pratiquement insoluble dans l'acétone et le benzène (1). Le produit est utilisé en général comme conservateur alimentaire et comme fongistatique en médecine, en particulier en dermatologie.

Selon M. Dersarkissian et Magda Goodberry, deux chercheurs qui ont étudié ses effets biologiques, le propionate de calcium représente une alternative à l'utilisation de produits fongistatiques toxiques et plus coûteux. Son efficacité comme fongistatique peut être comparée à celle du thymol, sans en avoir la toxicité (2).

En 1982 déjà, L. Santucci émit l'hypothèse de l'emploi du propionate non seulement comme fongistatique mais aussi comme désacidifiant du papier. Il envisagea en outre la possibilité de son utilisation dans des solutions alcooliques dans le cas où le document à désacidifier était écrit avec des encres solubles dans l'eau (3).

Expérimentation

Afin d'évaluer dans un premier temps l'efficacité de l'action désacidifiante du produit, on a effectué quelques essais en utilisant un manuscrit sans valeur dans lequel les encres étaient acides; une tache de couleur brune de nature inconnue était présente dans ce manuscrit. Les essais préliminaires ont été également répétés sur du papier acide d'un livre imprimé de 1929.

La concentration choisie de propionate pour les premiers traitements a été la même que celle indiquée par M. Dersarkissian et M. Goodberry pour un effet fongistatique: 5% dans de l'eau distillée. Les essais ont été ensuite répétés en utilisant une solution saturée dans de l'alcool éthylique. L'alcool méthylique n'a pas été retenu en raison de la toxicité de ce solvant dont l'usage est déconseillé dans les laboratoires de restauration.

Les valeurs mesurées du pH de surface (pH par contact) sont données dans le tableau I.

Tableau I. pH de surface d'échantillons traités et non traités avec du propionate de calcium (trois heures d'immersion)

Type de papier	non traité	traité 5% H_2O	traité avec une solution alcoolique
Whatman n.1	6,40	9,50	9,50
Manuscrit (bord blanc)	6,20	9,25	8,50
Manuscrit (tache sombre)	5,45	8,85	8,10
Manuscrit (encre)	5,40	8,60	6,60
Livre imprimé	4,20	8,70	6,60

Etant donné les bons résultats de la désacidification au cours des essais préliminaires sur des échantillons de papier ancien,

l'étude a été poursuivie en utilisant des échantillons de papier Whatman n.1 pour chromatographie afin de pouvoir étudier ainsi les effets du produit sur la stabilité de la cellulose.

Afin de simuler également l'effet que le propionate pourrait avoir sur des papiers oxydés, quelques échantillons de papier Whatman ont été oxydés, avant le traitement au propionate, avec de l'hypochlorite de sodium à différents pH (4). On a utilisé plus précisément les solutions oxydantes suivantes:

- 1- Solution d'hypochlorite à 1% (produit pur de Carlo Erba) à pH 12.
- 2- Solution d'hypochlorite à 1% neutralisée à pH 7 avec HCl.
- 3- Solution d'hypochlorite à 1% acidifiée à pH 2 avec HCl

La moitié des échantillons traités avec les solutions 1, 2 et 3 a été lavée à l'eau courante pendant une heure.

On a remarqué que les échantillons de papier Whatman oxydés à pH 7, non lavés et traités avec une solution de propionate de calcium, qui sont blancs à peine sortis de la solution, deviennent jaune-verdâtre au bout de 24 heures. Cette coloration disparaît ensuite après un lavage à l'eau. Il est possible que l'élément oxydant dominant à pH 7, l'acide hypochloreux, ait oxydé le propionate en formant des groupes chromophores. La facilité avec laquelle un simple lavage à l'eau enlève la couleur et la tonalité jaune-verdâtre renforce cette hypothèse. Il faut considérer néanmoins qu'aujourd'hui aucun restaurateur qualifié n'effectuerait un blanchiment avec de l'hypochlorite neutralisé, encore moins sans un lavage prolongé dans l'eau courante.

La moitié des échantillons traités et la moitié de ceux non traités ont été vieillis en chambre climatique à 80°C et à une HR de 76% pendant 10 jours.

Au cours du vieillissement, les échantillons traités avec le propionate se sont beaucoup moins assombris que ceux non traités. L'effet positif du traitement est particulièrement évident sur les échantillons oxydés, de pH 7 (photo n.1).

On a mesuré, sur tous les échantillons, le degré de blancheur (norme TAPPI 422), le pH (norme Aticelca MC 22), le degré de polymérisation moyen viscosimétrique (norme Afnor NF 12-005) et on a effectué les spectres IR (Perkin Elmer Infrared Fourier Transform Spectrometer) sur une pastille obtenue en mélangeant des fibres de papier avec du KBr.

Les résultats figurent dans les tableaux II, III, et IV. Les spectres les plus représentatifs (échantillons oxydés neutres, traités et non traités, avant et après vieillissement) sont reportés dans les figures 1, 2, 3 et 4.

Tableau II. Effet du propionate de calcium sur la blancheur du papier Whatman (un mois après le traitement).

papier	non traité		traité 5% dans l'eau		traité sol. alcool.	
	jours de vieill. 0 10		jours de vieill. 0 10		jours de vieill. 0 10	
Whatman	89	82	89	82	89	82
Whatman oxydé à pH 12	84	73	89	82	89	78
idem lavé	88	86	87	81	88	79
Whatman oxydé à pH 7	75	38	74	60	74	50
idem lavé	78	48	75	62	78	50
Whatman oxydé à pH 2	89	83	87	76	84	70
idem lavé	89	87	87	86	85	80

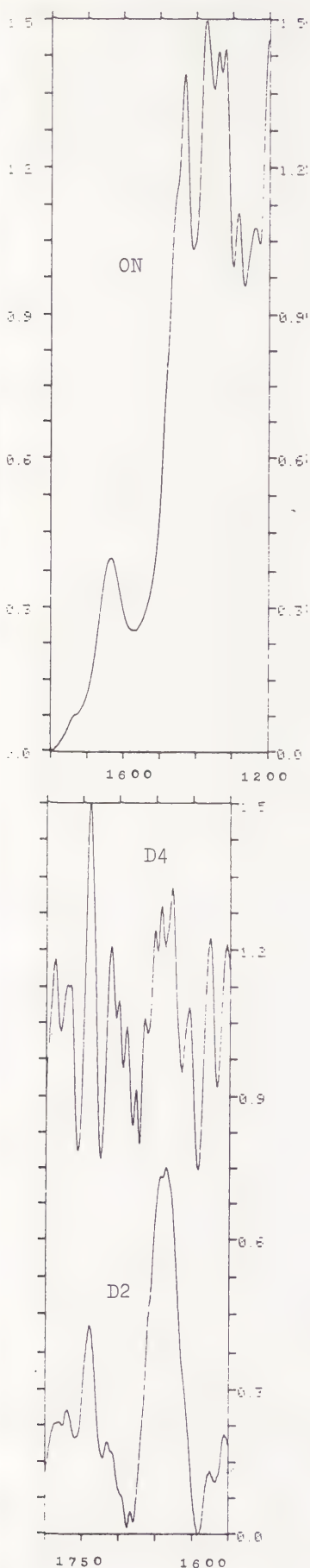


Fig.1
ON: spectre IR de papier Whatman oxydé à pH 7.
D2 et D4: le même en dérivée deux et quatre.

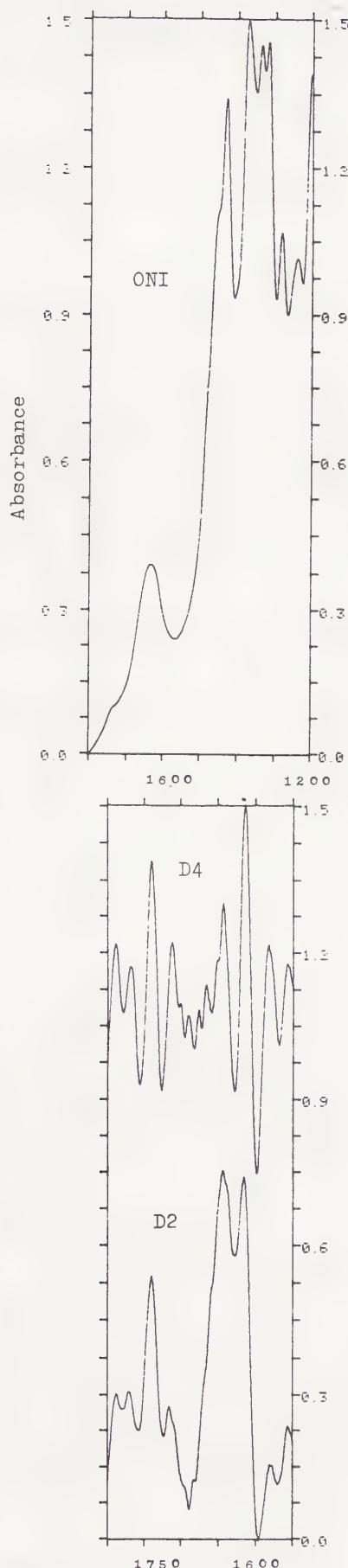


Fig.2
ONI: spectre IR de papier
Whatman oxydé à pH 7 et
vieilli.
D2 et D4: le même en
dérivée deux et quatre.

Tableau III. Effet du propionate de calcium sur le pH du papier
Whatman (un mois après le traitement)

papier	non traité		traité 5% dans l'eau		traité sol. alcool.	
	jours de vieill.		jours de vieill.		jours de vieill.	
	0	10	0	10	0	10
Whatman	5,9	5,3	9,3	8,6	9,1	8,7
Whatman oxydé à pH 12	8,6	7,3	9,1	9,2	9,2	9,0
idem lavé	8,1	8,0	9,0	9,2	9,0	9,0
Whatman oxydé à pH 7	6,0	5,8	9,2	9,1	8,0	7,9
idem lavé	5,4	5,3	9,1	9,0	8,1	8,0
Whatman oxydé à pH 2	5,0	4,9	9,0	8,9	8,4	7,9
idem lavé	5,4	5,2	9,0	8,9	8,0	7,9

Tableau IV. Effet du propionate de calcium sur le degré de
polymérisation moyen viscosimétrique du papier
Whatman.

papier	non traité		traité 5% dans l'eau		traité sol. alcool.	
	jours de vieill.		jours de vieill.		jours de vieill.	
	0	10	0	10	0	10
Whatman	1448	975	1386	1097	1447	1293

Discussion des résultats et conclusions

La mesure du degré de blancheur permet d'évaluer de façon objective ce que l'on avait déjà noté à l'oeil nu, à savoir l'effet positif du traitement au propionate de calcium, en particulier sur des échantillons oxydés dans un milieu neutre.

La mesure du pH a mis en évidence le bon pouvoir désacidifiant des solutions de propionate, même, bien que dans une moindre mesure, en solution alcoolique.

En ce qui concerne le degré de polymérisation on a remarqué, pour les échantillons traités avec le propionate et vieillis, une certaine difficulté à se dissoudre dans la cupriéthylène-diamine; ceci pourrait avoir faussé quelques mesures. Nous donnons quand même les valeurs de ces mesures auxquelles il faut accorder seulement une signification indicative. Les tableaux ne contiennent pas les valeurs de DP mesurées sur les échantillons oxydés: à cause de la présence, dans la molécule de cellulose, de nombreux groupes carbonyles, on assiste à une fragmentation ultérieure du polymère pendant la dissolution dans la solution alcaline de cupriéthylène-diamine; dans ce cas, la méthode de mesure peut amener à déterminer des valeurs de degré de polymérisation inférieures à la réalité. Cette hypothèse est étayée par le fait que, sur les échantillons oxydés de pH 7, on mesure un DP de 280 pour ceux non vieillis et de 200 pour ceux qui le sont, qu'ils soient traités ou non. Ceci est en contradiction nette avec le simple contrôle visuel des échantillons: les échantillons non traités apparaissent beaucoup plus abîmés que ceux qui sont traités.

Les spectres infrarouges de tous les échantillons présentent des différences seulement dans la partie comprise entre 4000 et 3000 cm^{-1} (bande de l'eau et des liaisons hydrogènes) et dans celle entre 1800 et 1500 cm^{-1} (bande de l'eau adsorbée, des carbonyles, des carboxyles, des liaisons doubles et des structures de type céto-enolique, di-cétonique, etc.) (5). La superposition de telles bandes rend extrêmement difficile l'identification des groupes fonctionnels responsables de la détérioration et de l'assombrissement.

Afin d'identifier ces groupes, nous avons élaboré les spectres avec la méthode de déconvolution en dérivée deux et quatre (D2 et D4), qui a mis en évidence des différences entre 1800-1500 cm^{-1} :

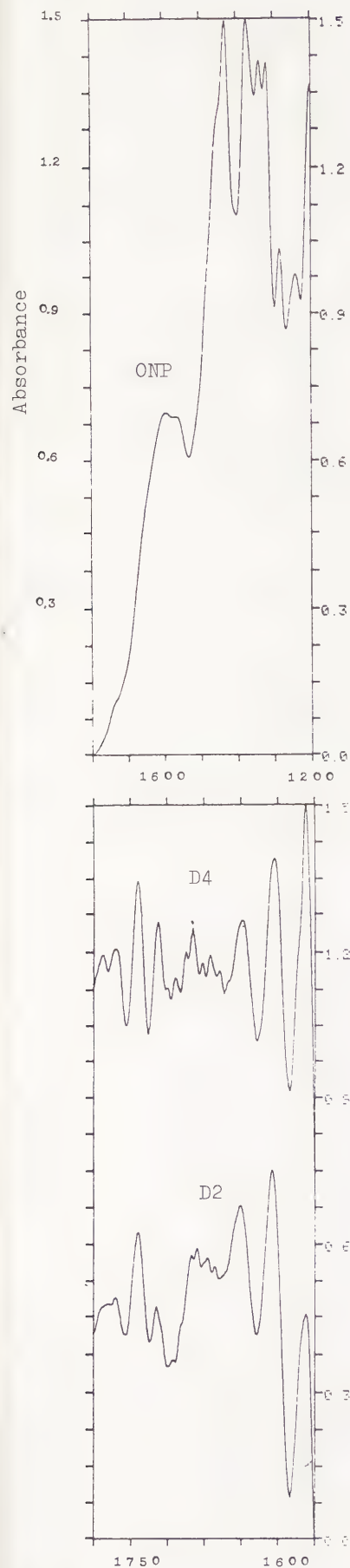


Fig.3
ONP: spectre IR de papier Whatman oxydé à pH 7 et traité avec le propionate.
D2 et D4: le même en dérivée deux et quatre.

- On peut observer que la bande à 1790 cm^{-1} , sur le papier oxydé avec l'hypochlorite dans un milieu neutre, a presque la même intensité avant et après vieillissement (échantillon ON et ONI), tandis qu'elle a une intensité plus basse sur les spectres relatifs aux échantillons traités avec le propionate, autant avant qu'après vieillissement (échantillons ONP et ONPI), et sur le papier Whatman témoin traité avec le propionate.
- La bande à 1740 cm^{-1} , relative aux groupes CO des carbonyles ou carboxyles, est présente dans tous les spectres de papier oxydé, mais elle est moins intense sur les échantillons traités avec le propionate.
- Entre 1700-1670 cm^{-1} on peut observer sur les échantillons ON et ONI des bandes multiples à faible intensité (évidentes en D4), moins évidentes sur les autres échantillons ONP et ONPI.
- Tous les papiers traités avec le propionate ont une bande très intense à 1665 cm^{-1} , absente dans les non traités et par conséquent typique du propionate.
- Autour de 1640 cm^{-1} une bande commune à tous les spectres, attribuable à l'eau, peut nettement être observée mais à des intensités différentes.
- La bande à 1610 cm^{-1} , faible sur l'échantillon ON, plus intense sur l'ONI, représentée par un petit épaulement dans l'ONP et d'intensité moyenne dans l'ONPI, est probablement attribuable aux liaisons doubles formées en plus grande quantité pendant le vieillissement sur le papier oxydé non traité que sur le traité.
- Tous les spectres présentent une bande à 1555 cm^{-1} très intense sur tous les papiers traités avec le propionate et donc probablement attribuable au propionate lui-même.
- Les autres bandes des spectres sont celles de la cellulose.

L'analyse avec la méthode de déconvolution permet de supposer qu'il existe une certaine action stabilisante (visible à l'œil nu) du propionate de calcium sur les échantillons oxydés avec l'hypochlorite de sodium. L'attribution des bandes d'absorption aux groupes fonctionnels est encore en phase d'étude dans notre laboratoire (6), toutefois ces premiers résultats sont très encourageants. La possible utilisation, encore à vérifier complètement, du propionate de calcium comme fongistatique, désacidifiant et stabilisant, serait extrêmement intéressante.

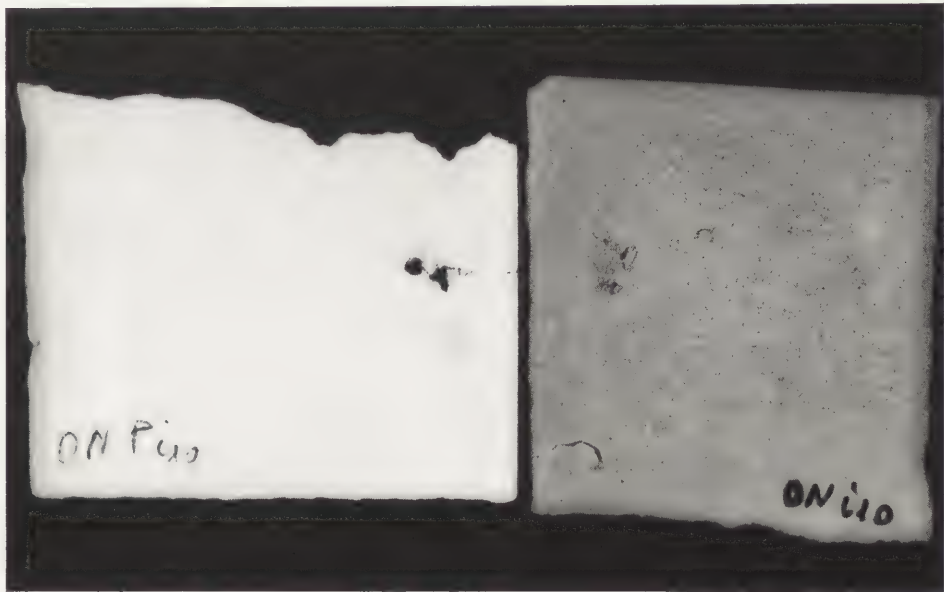


Photo n.1

- ONPi10: papier Whatman oxydé à pH 7, traité avec le propionate de Ca et vieilli à 80°C et 76% HR pendant 10 jours.
- ONi10 : papier Whatman, oxydé à pH 7, non traité, vieilli à 80°C et 76% HR pendant 10 jours.

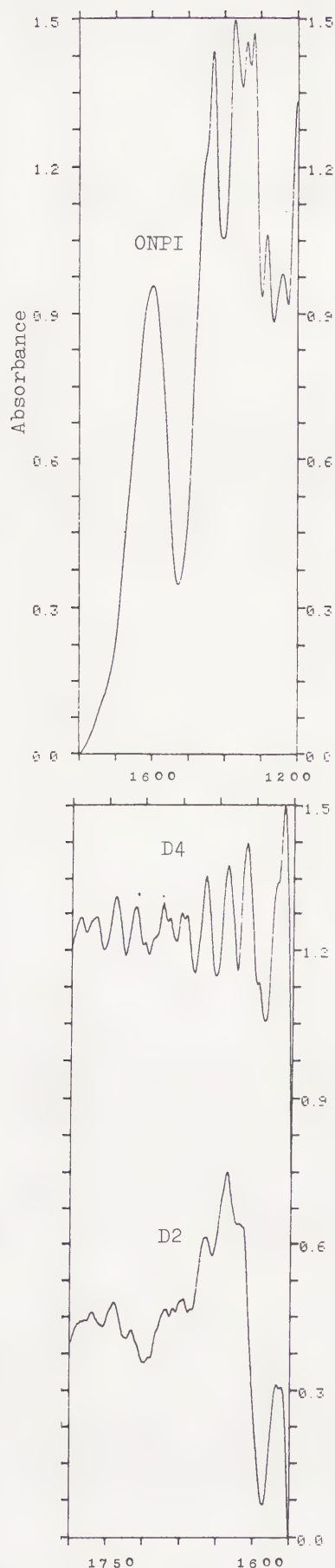


Fig.4

ONPI: spectre IR de papier Whatman oxydé à pH 7, traité avec le propionate et vieilli.

D2 et D4: le même en dérivée deux et quatre.

Références

1. The Merck Index, (Rahway, N.J.: Merck & Co., 1976), 1969.
2. M. Dersarkissian and M. Goodberry, "Experiments with non toxic anti-fungal agents", Studies in Conservation, 25, No. 1 (1980): 28-35.
3. L. Santucci, "Insecticidas y fungicidas para libros y documentos. Tratamiento y sus efectos", in "Memoria del Primero Seminario Internacional de Conservacion de Documentos, Libros y Materiales Graficos, Informacion de Archivos, 20, (1983): 42-57.
4. A. Linardy and P. Van Damme, "A Bibliographical Survey of the Bleaching of Paper", Restaurator, 9, No. 4, (1988): 178-198.
5. R.G. Zbankov, Infrared Spectra of Cellulose and its Derivatives (New York: Consultants Bureau, 1966), 117-130.
6. P. Salvini and G. Martinelli, "Numerical Processing of Fourier Transform Infrared Spectra/ A Powerful Tool in Paper Analysis", (rapport présenté a cette Conférence).

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Working Group 15

Mural Paintings and Mosaics

Peintures murales et mosaïques



ABSTRACT

The Romanesque mural paintings of the Salzburg Nonnberg were endangered by pulverisation of the paint layer and the growth of microorganisms. Although the interdisciplinary examinations carried out recently have not been completed, first urgent steps had to be taken to create the conservation of the mural painting in situ.

A new method of a reversible fixation with Hydroxipropylcellulose HPC Klucel LF has been developed, combined with the climatisation of the site.

THEORY AND PRACTICE. REMARKS TO THE EXAMINATION AND CONSERVATION OF THE ROMANESQUE MURAL PAINTINGS IN SALZBURG NONNBERG

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1. Methodological premise

Conservators of mural paintings are often confronted with the situation, that urgent steps must be taken for conservation of an object. The decision on the use of materials and methods of conservation must often be made before the material qualities and the dynamics of the mural paintings deterioration processes have been discovered in detail. As a result the normal requirements for a logical choice of intervention methods based upon analytic results, sometimes remain abstract, and in this sense only theoretical.

The possibilities of analysis and of intervention by the conservator are not only subject to the practical working conditions, but also to the historical development of experience of conservation. In this sense every step of conservation can be understood as an open ended process of recognition. The contradiction between the discovery potential and the necessity for practical work remains in the care for historical monuments - as in all aspects of social activity - an ongoing phenomenon. Successful conservation treatment can be understood as a dialectic synthesis of this contradiction and at the same time its reproduction on a new level.

Taking these considerations as a starting point the examinations and interventions of the Romanesque mural paintings of the church of the benedictine nunnery Nonnberg in Salzburg may be summarised as follows.

2. History of conservation

The mural paintings, which date back to the early second half of the 12th century belong to the "paradigmatic works of the high Romanesque epoche" according to O. Demus (2, p. 97). They are the remains of the decoration of the western part of the Romanesque basilica founded at the end of the 7th century. They are located on the west and north wall of an area, which probably represented the former "paradise", the area between west tower and long house.

Due to the construction of the nuns choir after the fire of 1423 the mural paintings were partly hidden by walls and confined in an area which was closed off to the public. As a result, they were spared the climatic fluctuations of the church. This type of situation could play an essential part in the conservation of the mural paintings for over 700 years.

In 1894/95 the supporting structure of the nuns choir was opened to the east by the formation of arcades. Thus the murals were accessible again but at the same time they became subjected to the changing climate within the church.

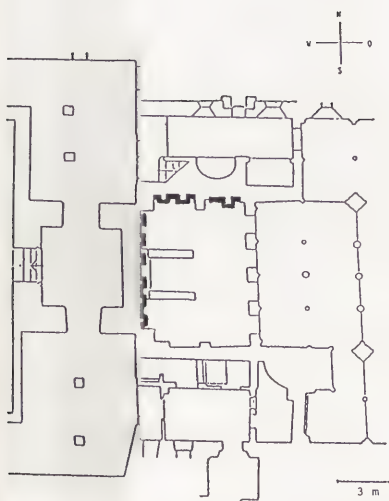
According to old photographs the mural paintings were already undergoing a slow process of deterioration before 1894 and probably at this time the paint layer was refixed using an organic fixative.

In spite of disinfection using formaldehyde in 1955 and cleaning procedures the further development of microorganisms could not be stopped. In the last decades the deterioration process began to greatly threaten the paint layer.

In 1977 the painting of the second niche (St. Augustinus) was detached and transferred onto a sandwich support made of glassfiber-polyester (executed by S. Enzinger). At the same time the foundations were aired by digging down one metre until the rockbed was reached.

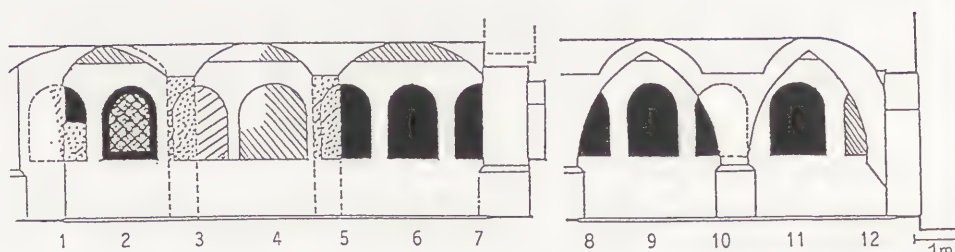
The aim of our recent examinations was to create the conditions for the conservation of the mural paintings on site. The wall paintings atelier of the conservation department of The Bundesdenkmalamt (Federal Office for Monuments and Sites) have started research into the structure and climate, as well as the painting technique and the phenomena and causes of damages, in collaboration with the chemical laboratory and the architectural department of The Bundesdenkmalamt. Advice from national and international scientists and conservators was also sought.

More than a third of the mural paintings have pulverised, mostly as a result of the crystallisation of soluble salts. The total visible area of about 30 m² is contaminated by microorganisms, mostly bacteria and fungi.



Salzburg Nonnberg situation of the wall paintings

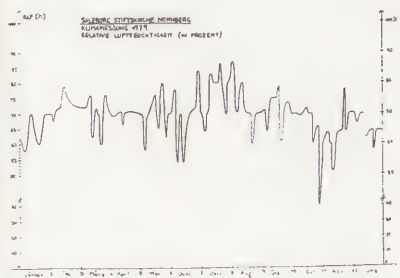
- open in 1857 (cf.G.Heider, 1857)
- ▨ opened in 1894
- ▧ opened in 1894 (without mural painting)
- ▩ opened in 1955 (cf.W.Frodl, 1956)
- ▦ detached in 1977



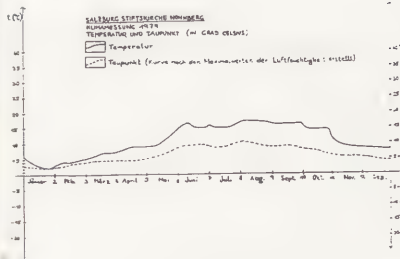
Salzburg Nonnberg monastery church, former "paradise", romanesque wall paintings. Chronology of opening of the niches. Niche 1-7: west wall, niche 8-12: north wall



Niche 4 (St.Benedictus) before intervention (1988)



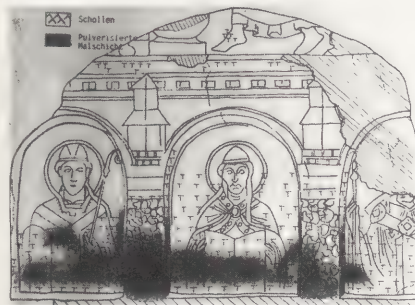
Salzburg Nonnberg, "paradise"
relative humidity 1979
(maximum rates)
BDA/ Hudetz



Salzburg Nonnberg, "paradise"
room temperature and dew point
BDA/ Hudetz



Reconstruction of niche 6.
Aquarell on paper
BDA/ Podgorschek 11/89



Niches 5-7. Pulverisation
of paint layer
BDA 12/87

The conservation method was developed together with the free lance restorer Ernst Lux, in the context of a pilot work (niche 5-7). This has not yet been completed. E.Lux is also involved in the further conservational steps concerning the remaining areas (niches 1-4 and 8-12).

3. Examination and documentation

The examinations were carried out through interdisciplinary work. The material, technique and architecture and the painting including the history of its creation and the history of its conservation were examined. Restorers carried out investigations into the physics of the structure as well as phenomenological research of the condition and deterioration of the painting and its support. These examinations were completed by laboratory analysis (H.Paschinger, H.Richard, Riedl, Bauer). As a result of this research a plausible explanation of the deterioration processes and their causes was given in spite of the fact, that the results were not based on scientific analysis to the last detail. A number of questions remain open. However, the conservation methods, so far successfully completed, have empirically confirmed the research and its resulting conclusions.

3.1. Architecture

The architecture, supporting the mural paintings is older than the paintings themselves. From the sequence of the white wash layers and the style of the building it could easily date back to the 11th century. The wall structure consisting of untreated stones, built up in the customary method filling the interior space between two walls, consists of geologically different materials with varying porosity. The structure of the original space, the former "paradise", is not reconstructable at the present time. Underneath the vaults of the nuns choir of the 15th century the mural paintings partly continue. The possibility of further remains of the mural paintings in the area of the western wall of the nuns choir will be investigated. The mural paintings begin approximately 2 metres above the natural rock on which the building is founded.

3.2. Painting technique

Due to the overlapping rendering, the surface structure and the features of deterioration, the execution of the mural paintings using the secco technique can be deduced (Kalkseccomalerei). The sequence of layers of the incarnation in particular reveals a surprising concordance with the codification given by Theophilus.

The mural paintings have lost a great deal of their original exquisite colouring and richness of contrasts (cinnabre, lapis lazuli), on the one hand due to loss of parts of the paint layer and on the other hand due to colour changes. The cause of these processes has not yet been completely investigated.

The original colour impression of these paintings was reconstructed in a copy carried out in aquarelle on paper (by Claudia Podgorschek). This was constructed on the basis of examining the layers of well preserved parts and by comparing them with related illuminated manuscripts as well as by traces and measurements through which the technical construction could be taken into account (snapping cord, compass marks and crescents, and engravings).

3.3. Phenomena of deterioration

More than a third of the mural paintings were pulverised before fixation. In several places scaling was discovered, especially in the lower parts of the niches.

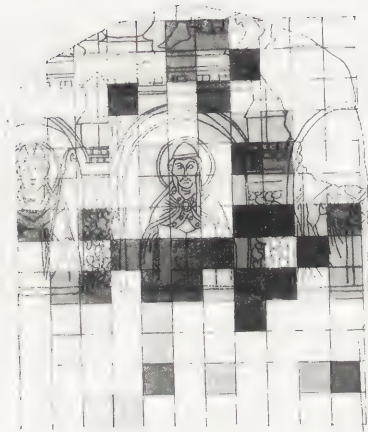
It was unusual to see that there were rows of bacteria in the form of small chains of pearls settled along the brush strokes. The substrate for these microorganisms is presumably a layer of organic glue, which was applied for fixation probably in 1895. Empirically it seems to be skin glue, but chemical analysis indicates that casein or egg cannot be excluded.

Apart from those bacteria, which have not yet been categorised, we have found a number of fast growing fungi, which can be found everywhere in the air and on the ground (sugar fungi). These are not specified fungi for painted objects. In addition to these there are small insects, which feed on the microorganisms.

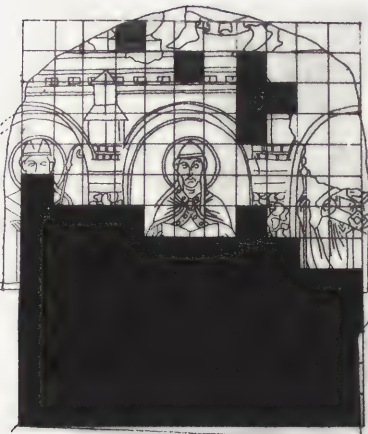
From the beginning of the examination the microorganisms were spread out in an irregular manner. This could indicate inconsistent periods of condensation humidity. It would appear, that they are concentrated in the lower area but reach up to the height of the niches in coordination with the former fixation. All the mural paintings are sensitive to water including in those areas which are not contaminated with soluble salts and have few microorganisms.



Niches 5-7. Microorganisms
BDA 12/87



Niches 5-7. Electric capacity (MOISTURE MONITOR M 49; High)
180C, 71% rh; 17.10.1989
BDA/ Ha/Pr/Ve



Niches 5-7. Electric conductivity, (PROTIMETER surveymini II, 1-10)
180C, 71% rh; 17.10.1989
BDA/ Ha/Pr/Ve

Naturally the accumulation of dirt was particularly severe at the pulverised parts. Paint particles were just attached to the threads of the microorganisms. Due to former cleaning the layer of dirt was irregular. On impasto parts the colour had been rubbed off. It was not always easy to differentiate between the whitish layer of microorganisms and the salt efflorescences. The salts consist of nitrates and chlorides (3:1) and few sulfates. The salt content is "critical" at the level of 2%. Samples of only a few areas have been taken for analysis.

3.4. Physics of structure - causes of deterioration

The climatic measurements which were taken at the beginning with a thermohygrograph and whirl psychrometer and later with an electronic system, showed that in the winter (the second half of January until mid March) the maximum relative humidity (rh) came very close to the saturation point. These measurements were taken, while the arcades were still open, that is before the climatisation of the space. One had to take into account the thermal condensation of humidity, particularly towards the end of the cold period and the also colder walls.

Measurements of the absolute humidity in the wall at various levels (humidity profile), taken under the wall of the niches and on the back of the painted walls, showed a reduction of humidity from the exterior to the interior, which indicates condensation humidity. The measurements were taken according to the calcium carbide method. The existence of condensation processes was also confirmed by the results of the measurement of the electric conductivity, using a PROTIMETER, surveymini II. Higher values were measured when higher air-temperature or higher relative humidity arose. Furthermore, increasing values in the lower area of the niches, which can be defined as the level of the crystallisation of soluble salts, became apparent. These results can be taken as proof of hygroscopic condensation, which is especially caused by hygroscopic salts. Further irregularities of our results could be connected to hygroscopic organic substances on the surface (glue of the former fixation and microorganisms).

Further measurements, taken over a period of several years proved, that the digging of 1977 had a distinct drying effect. Due to this the level of crystallisation of soluble salts changed. It would seem that this process is a central cause for the acceleration of the deterioration process over the last 10 years.

A special case is the deterioration process reaching up to the vault in the area of the niches 1 and 2. Here the effect of a long term water infiltration in the area of the long house gable, which is situated 13 meters above the mural paintings, cannot be excluded. This is due to the wall's construction containing a lot of holes in the interior.

4. Results of the recent interventions

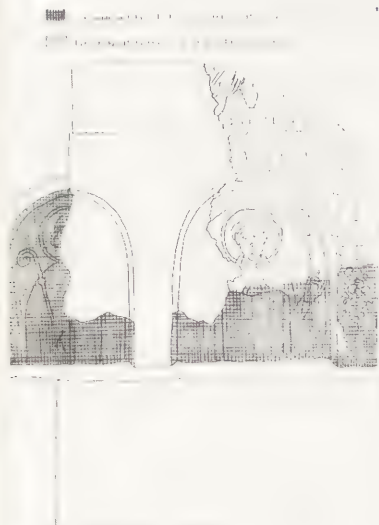
4.1. Climatisation

In order to prevent further crystallisation of soluble salts, the area under the nuns choir, the former "paradise", which contains the mural paintings, was climatised. The arcades, which had been opened in 1894, were reclosed provisionally using wooden laths, polyethylene sheets, polyurethane-foam mats and boards of pressed cellulose. In this way the space was isolated and granted its own air circulation and thermal conditions away from the remaining church space. Thus a physical situation was reconstructed, which had existed before the opening of the arcades in 1894.

After an adjustment phase the climate reached a level of 70% rh and approximately 150 C. Similar to the conservation of the romanesque mural paintings in Lambach/ Upper Austria (about 1090), which were also carried out between 1979 and 1981 by the conservation department of The Bundesdenkmalamt, the crystallisation of the soluble salts could be prevented. The electronic adjustment of the humidifier is set at 67,5% rh. This percentage was empirically found to be the minimum level for the solution of the salts. No heating is necessary.

4.2. Disinfection

The high relative humidity at a heightened temperature in the former "paradise" present favourable conditions for the development of microorganisms. The balance created by the climatisation can only be preserved by disinfection, at the beginning repeated approximately every 4 weeks. We used Thymol as the disinfection media, dissolved in acetone and demineralised water (1:1), approximately 2%. Alcohol is excluded as a solvent in order to avoid an additional growth of microorganisms. The water content of the solvent has to prevent a rapid evaporation and a likewise rapid crystallisation of soluble salts.



Niches 3 and 4. Areas fixed with Japanese paper and KLUCEL LF, 2% in alcohol



Niche 6, detail. After cleaning, with campione showing the layer of dirt.
BDA/ Jöbstl

4.3. Fixation

The overlaying dirt and the microorganisms can be separated from the paint layer only, if the fixation is reversible. Therefore a mineral fixation, which is not reversible, was excluded. The use of artificial resins such as acrylics was also excluded with regard to the physical processes of the structure. The drying effect which is caused by a solvent is also undesirable. After a phase of examination and consultation, we chose hydroxy propyl cellulose (HPC, KLUCEL LF), approximately 2% diluted in alcohol.

The fixation of the paintings was started in July 1988 in the area of the niches 5-7 (pilot work). In December 1988 the rest of the mural paintings of the western wall (niches 1-4) were fixed. At the northern wall the deteriorated area is considerably smaller, particularly in relation to the small amount of pulverisation due to crystallisation of soluble salts. Therefore we omitted the fixation of these areas for the moment. This is justifiable only if the climatisation is working and the disinfection is repeated periodically.

One of the advantages of the HPC is its seemingly biostatic effect. Further contamination of microorganisms could not be discovered in the areas where the fixation with HPC has been executed. We had to disinfect these areas again after the cleaning, i.e. the partial removal of the HPC.

The fixation media was initially sprayed in an extremely very dispersed aerosol. In this way we succeeded in replacing those particles of the paint layer, which had been dislocated to some extent. The fixing with fine Japanese paper was executed only on the pulverised and sensitive parts. In the upper parts of niche 4 we omitted the facing because the paint layer was in a better state of conservation.

4.4. Cleaning

After the fixation the layers covering the paint and the paint layer itself were linked with the same glue. Therefore the covering layers had to be removed in a controlled fashion, layer by layer. The fixation media incorporated favourable characteristics for this process. It was also used for cleaning in the following composition:

40ml KLUCEL LF OR MF, 2% in alcohol
20ml alcohol
1-4ml demineralised H₂O

To get a higher viscosity of the cleaning media, the content of HPC was increased. We used more water or even some ammonia to remove dirt, which seemed to be linked stronger to the fixation (1:1, sometimes with 10% ammonia). The superfluous HPC was removed with alcohol using a fine brush or cotton and cellulose sheets. In the process of cleaning, the fixation is limited first to the surface. This is due to the viscosity and thixotropic effect of the cellulose (HPC). In the same time the HPC as cleaning media forms an emulsion of the dissolved layers covering the paint layer. In this way we get a gliding effect similar to the saliva, which prevents the violation of the paint layer during the process of the cleaning and helps to remove the dirt in thin layers. To prevent the swelling of the proteins of the former fixation glue (from 1895?) we used alcohol instead of water.

In the first step of conservation the cleaning was executed only as far as it seemed necessary for the maintenance. The "patina", remained intact. The former aqueous consolidant can only be removed, if it is substituted by a non aqueous fixation media. On the other hand, this fixation is the substrate of the microorganisms and had to be removed - or intoxicated.

A change of colour caused by the fixation media (HPC) was not observed.

5. Conclusions

A helpful, but not very large space of time has been gained through the completion of urgent conservational steps based on examination and documentation up until now. One of the most important justifications of conservational techniques is their relative reversibility. But the situation is finely balanced. Further losses can be prevented only by a continuous, very time consuming control of the status quo and by repeated disinfection.

Now appropriate methods for the reduction of soluble salt concentrated on the paintings' surface, for a permanent (or at least more "permanent") disinfection, and also an improvement in the condition of the physical structure of the space must be found. Such methods can be found using results of further examinations concerning still unanswered questions relating to the architecture, painting technique, deterioration processes and conservation methods carried out up until now (HPC KLUCEL, cleaning, disinfection).



Niche 6. Cleaning procedure
BDA/Jöbstl

6. Bibliography

1. O.Demus, Romanische Wandmalerei, München 1968
2. B.Bischoff, S.Waetzold, H.Roosen-Runge, Quellengeschichtliche Untersuchungen zur "schedula diversarum artium" des Theophilus, in: Münchner Jahrbuch der Bildenden Kunst, III. vol. III/IV 1952/53, p.145-171
3. P. and L.Mora, P.Philippot, Conservation of Wall Paintings, London etc.1983 (french: Bologna 1977)
4. G.Torraca, Dangers présentés par l'utilisation des produits synthétiques pour les oeuvres d'art et pour les restaurateurs. Produits synthétiques pour la conversation et la restauration des oeuvres d'art, 1ère partie, Berne 1987, 41-55
5. I.Hammer, Organisch oder anorganisch? Probleme der Konsolidierung und Fixierung von Wandmalerei, in: loc.cit. (Restauratorenblätter 9), p.89-97
6. idem, Zur in situ Konservierung der romanischen Wandmalereien der Stiftskirche Lambach, in: loc.cit. (Restauratorenblätter 9), p.89-97
7. idem, Sinn und Methodik restauratorischer Befund-sicherung. Zur Untersuchung und Dokumentation von Wandmalerei und Architekturoberfläche, in: loc.cit. (Restauratorenblätter 9), p.34-58
8. G.A.Berger, Formulating adhesives for the conservation of paintings, in: N.S.Bromelle, and P.Smith (eds), Conservation and Restoration of Pictorial Art, London etc. 1976, p.169-181 (KLUCEL J)
9. J.Hofenk de Graaff, Hydroxi propyl cellulose, a multi-purpose conservation material, in: ICOM Committee for Conservation, Ottawa 1981/14/9 (KLUCEL 6)
10. G.Banik, M.Ranacher, Alkohollösliche Zellulose. Information 16, in: Restauratorenblätter 6 (ibidem), Wien 1982, p.144 s. (HPC H - E)
11. R.C.Wolbers, Notes for Workshop on new methods of the cleaning of paintings, Getty Conservation Institute, August 15-25, 1988 (not published; HPMC, saliva)



Niche 6, detail, UV-foto
BDA/ Roschnik

RESUME

Le présent rapport concerne les problèmes de refixage des supports d'enduit en y injectant de la matière liante et fait état des propriétés technologiques des composés à injecter à base d'un véhicule calcaire. On démontre la possibilité d'une utilisation efficace de superplastifiants en vue d'améliorer les caractéristiques technologiques et d'utilisation des mortiers de chaux. On offre aussi les composés et les performances de nouveaux véhicules utilisés pour l'injection.

MOTS-CLES

refixage par injection, viscosité, charge minérale, complexes anionactifs, superplastifiants, chambre climatique

LES NOUVELLES METHODES DE REFIXAGE PAR INJECTION DANS LES SUPPORTS D'ENDUIT DES PEINTURES MURALES

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U R S S

Introduction

Le problème de refixage par injection des supports d'enduit des peintures murales anciennes russes est actuellement, en dépit de son acuité, peu étudié par les scientifiques. Ceci s'explique par le fait que le nombre de restaurateurs et de chercheurs s'intéressant à ce problème est très restreint, que ce problème de rigueur manque d'attention voulue. L'expérience acquise dans ce domaine exige une analyse sérieuse et une interprétation scientifique du problème dans son ensemble compte tenu des derniers succès dans le domaine de la chimie de liants minéraux. Cela est d'autant plus nécessaire que les exigences respectives, nettement formulées, concernant la composition de médiums à injecter, sont encore absentes, ce qui réduit la possibilité d'élargir leur assortiment. L'analyse de maigres publications consacrées à ce problème permet d'en déduire que ce ne sont que des comptes rendus qui concernent des travaux pratiques exécutés sur tel ou tel autre monument où on s'est servi du médium d'une composition appropriée. Comme on le voit l'utilisation des produits d'injection se réduit actuellement à deux espèces de véhicules dont l'un a une composition purement calcaire et l'autre, une composition caséino-calcaire. Il y a encore un fait à noter: les recommandations de divers auteurs utilisant des liants de composition identique diffèrent. Ceci concerne le temps de maintien préalable de la pâte de chaux aussi bien que le rapport entre les composants principaux (pâte de chaux, caséine, eau, matériau de remplissage) d'un véhicule donné à injecter. Les contradictions existantes s'expliquent, selon D. E. Briaguine, par le degré de l'état de conservation d'un enduit à refixer; cela contraint les restaurateurs à varier les rapports entre les principaux composants en partant de leur propre savoir, leur expérience et intuition. Une telle façon subjective d'aborder le problème de refixage par injection des supports d'enduit est due à l'absence totale de recherches de laboratoire dans ce domaine. Les rapports entre les composants de départ d'une solution à injecter sont choisis par les restaurateurs lorsqu'ils sont en train de réaliser des travaux sur des monuments uniques de la peinture murale ancienne russe, ce qui les prive de la possibilité de pronostiquer la qualité de refixage et ce qui rend imprévisible le résultat du travail. Une telle approche conduit à des conséquences déplorable, ce qui est facile à prouver par de nombreux exemples concernant les monuments bien connus.

A vrai dire, il est très difficile de conférer à un véhicule à injecter des paramètres voulus tels que la viscosité de départ, la perte de volume pendant le durcissement et la durabilité de la résistance adhésive, ne partant que de sa propre expérience et de son intuition. A noter que dans ce cas-là plusieurs recommandations de caractère qualificatif (par exemple: "Le mélange/ c'est-à-dire la solution à injecter/ ne doit pas être très liquide ni trop dense, il doit être maniable pour qu'on puisse le verser facilement en se servant d'une poire de caoutchouc munie d'un embout spécial.") ne seront pas en mesure de rendre service.

Seules les recherches de laboratoire visant la détermination quantitative d'exigences technologiques émises aux solutions à injecter permettront d'éviter tout subjectivisme, d'optimiser les composés connus et d'élaborer des médiums plus efficaces. C'est dans ce sens que poursuivent leurs recherches les collaborateurs de la section de la restauration de peintures murales du VNIIR. Les résultats de ces recherches sont donnés plus bas.

Les principales exigences auxquelles doivent répondre les solutions à injecter sont, à notre avis, les suivantes: une basse viscosité de départ permettant de l'injecter facilement à l'aide d'une seringue ou d'une poire, une perte insignifiante de volume pendant le durcissement et un caractère stable de la valeur de résistance adhésive dans le temps.

A première vue les deux premières exigences semblent fort simples; néanmoins, leur satisfaction simultanée dans un composé donné se révèle assez compliquée. Cela s'explique par le fait que pour diminuer la viscosité de départ de la pâte de chaux, composant principal de la solution à injecter, on a recours à une

simple dilution avec de l'eau. Ce faisant, les restaurateurs, ne pouvant pas contrôler la viscosité de départ, le font à l'oeil nu en se basant sur leur expérience et leur intuition. Cependant il est notoire que plus grande est la quantité d'eau dans un mortier de chaux, plus grande est la valeur de perte de volume pendant le durcissement. Alors, cherchant à diminuer cette perte de volume, les restaurateurs introduisent dans les solutions à injecter une charge minérale et, par ceci, ils augmentent de nouveau la valeur de viscosité de départ de la solution. Ainsi, en expérimentant chaque fois sur un monument, le restaurateur se voit négliger une des deux premières exigences en fonction de la situation. Cette façon de résoudre le problème exclut absolument la prise en considération de la troisième exigence qu'on impose aussi aux solutions à injecter. Voilà pourquoi le processus de refixage par injection des supports d'enduit s'avère comme celui qui demande beaucoup de main d'oeuvre, ou bien, dans un certain temps, on voit qu'une portion d'enduit refixée commence à s'écailler et s'accompagne de destructions supplémentaires.

Comme il est dit plus haut, la tâche la plus urgente que nous avons avancée pour résoudre l'ensemble du problème, consiste à optimiser, en fonction de l'injection à faire, la valeur de viscosité de départ d'une solution à injecter. Ce faisant, il est nécessaire de trouver un procédé efficace qui permettra au restaurateur, qui est en train d'accomplir les travaux de restauration sur un monument, d'effectuer, d'une manière sûre et simple, le contrôle de la valeur de viscosité de départ et, en fonction de cela, faire un choix bien motivé du rapport entre les principaux composants. La détermination de la valeur optimale de viscosité de départ de la solution à injecter s'est opérée comme suit. On diluait la pâte de chaux de consistance normale avec des quantités d'eau toujours croissantes. Ensuite, les sept restaurateurs participant à l'essai ont échangé leurs avis pour chaque échantillon. On a ainsi trouvé une consistance qui satisfaisait visuellement tous les participants à l'essai. L'échantillon choisi a été soumis à l'étude avec un viscosimètre "Rhéotest-2". D'après les résultats de l'essai on a établi que la valeur de viscosité, qui satisfaisait tous les restaurateurs, constituait de 750 à 800 MPa.s. cette valeur a été prise comme une valeur optimale pour notre solution à injecter.

Pour que le contrôle de la viscosité dans des conditions pratiques soit plus facile on a décidé de soumettre l'échantillon choisi aux mesures à l'aide d'un appareil viscosimétrique très simple "B3-4" qui représente un entonnoir plastique de 100 ml de capacité avec un orifice de sortie de 4 mm. La durée d'écoulement de la solution (plus précisément de tout le volume indiqué) caractérise en secondes sa viscosité. D'après l'appareil "B3-4" on a établi que la viscosité optimale de la solution à injecter constituait de 20 à 22 s.

Ainsi, on a réussi, pour la première fois, à exprimer quantitativement la valeur optimale de la viscosité de départ de la solution à injecter, ce qui permettait d'optimiser les rapports entre les composants des produits déjà connus et ouvrait les possibilités pour la recherche de nouveaux composés plus efficaces.

En effet, simultanément avec l'élaboration de nouveaux composés d'injection, nous avons, pour la première fois, étudié les propriétés rhéologiques du composé caséino-calcaire, optimisé les rapports entre ses principaux composants et la technologie de sa confection, compris le mécanisme d'action qu'exerce la caséine sur la structure et les propriétés d'utilisation du mortier de chaux.

La recherche dans le sens de création de nouveaux composés d'injection se faisait par la voie d'élaboration de procédés efficaces visés à diminuer la viscosité de départ des mortiers de chaux et, simultanément, la quantité d'eau utilisée. De nombreuses publications indiquent qu'un des procédés permettant de réduire la tension superficielle des mortiers consiste à y introduire des matières superficiellement actives. Ces derniers temps, à titre de ces derniers ont reçu une large utilisation dans l'industrie de la chimie de liants minéraux les dérivés de cellulose et, notamment, la cellulose de méthyle oxyalkoylée qui représente une poudre cristalline bien soluble dans l'eau.

On a étudié l'influence des solutions aqueuses de cellulose de méthyle oxyalkoylée sur les propriétés rhéologiques de la pâte de chaux de consistance normale. Les résultats de recherches nous ont conduit à la conclusion que pour obtenir une diminution maximale de viscosité la concentration optimale de la solution de cellulose de méthyle oxyalkoylée (CMO) doit être à un pour cent.

Les recherches concernant l'influence quantitative de la solution CMO à un pour cent sur la viscosité de la pâte de chaux de consistance normale ont démontré que la valeur voulue de viscosité de départ pour un composé à injecter (de 750 à 800 MPa.s) est obtenue à un rapport suivant: pâte de chaux: 10 CMO = 2 : 1. Cela faisant, l'introduction de la CMO permet de diminuer de 4 fois la contenance en eau, ce qui contribue à son tour à une brusque diminution de la valeur de perte de volume durant le durcissement d'un tel composé d'injection. L'étude du mécanisme d'action de la CMO sur la structure de la pâte de chaux prouve que la CMO, étant de par sa nature un plastifiant structural, n'entre pas en interaction chimique avec un liant calcaire, mais remplit des zones structurales défectueuses durant son durcissement. Par ceci on obtient une amélioration considérable de la structure d'un composé d'injection durcissant. Comme l'ont montré les résultats des recherches effectuées, ce fait a contribué à améliorer la résistance adhésive des composés d'injection avec des surfaces jointes (voir le tableau 1).

L'essai pratique d'un composé calcaire avec la CMO à titre de solution à injecter fut réalisé en 1985 pendant les travaux de refixage sur le support de l'enduit écaillé dans l'église de Saint-Jean-le-Théologien dans la ville de Rostov Vélikii.

L'examen visuel de la portion refixée, fait en 1988, n'a pas révélé de destructions et d'écaillages de l'enduit.

L'élaboration de complexes anionoactifs spéciaux, dits superplastifiants (SP), représente une des dernières acquisitions dans la chimie de liants minéraux. Les SP représentent des liquides incolores parfaitement solubles dans l'eau. Possédant des propriétés des matières superficiellement actives les SP améliorent considérablement les propriétés technologiques des composés de ciment dans la production des matériaux de construction.

Nous avons étudié la possibilité d'utilisation des SP en vue de diminution de la viscosité de départ de la pâte de chaux dans l'intention d'élaborer de nouveaux composés d'injection. A cet effet nous avons utilisé trois types de SP. Premièrement nous avons estimé l'influence des concentrations de solutions aqueuses des SP sur la viscosité de la pâte de chaux de consistance normale. Les résultats ont prouvé qu'on obtient l'effet maximum de diminution de viscosité pour tous les types de SP lorsqu'on utilise des solutions à un pour cent. Ce faisant le rapport optimal était le suivant: 70 g de pâte de chaux de consistance normale + 20 ml de la solution à un pour cent de SP. En étudiant les propriétés rhéologiques des solutions calcaires avec divers SP on a établi que le produit avec SP-1 a la viscosité de départ égale à 700-750 MPa, tandis que les produits avec SP-2 ou SP-3 ont la viscosité de 20 à 250 MPa.s. Pour améliorer les propriétés d'utilisation d'un composé à injecter en cas d'obtention d'une valeur de viscosité de départ inférieure à celle voulue à l'introduction des SP-2 ou SP-3 il faut y introduire un charge. A titre de charge nous avons utilisé CaCO_3 , réactif livré par l'industrie qui représente une poudre blanche finement dispersée dont la surface spécifique est égale à $145 \text{ m}^2/\text{kg}$.

Les essais ont permis de constater que l'introduction dans la solution calcaire avec SP-2 ou SP-3 de la charge CaCO_3 (le rapport étant le suivant: la pâte de chaux de consistance normale: CaCO_3 = 2:3) conduit à une diminution de la perte de volume de 2 à 3%. Et bien que la viscosité de départ du produit augmente grâce à l'introduction de la charge de 200-250 MPa.s jusqu'à 600-650 MPa, elle ne dépasse pas pourtant une valeur voulue pour la solution à injecter (750-800 MPa.s).

Pour déterminer l'influence des SP sur la structure d'un liant calcaire on a procédé à toute une série de recherches en recourant à la spectroscopie infrarouge, la spectrophotométrie, l'analyse thermique différentielle, la microscopie électronique et l'analyse électrophorémétrique. On a constaté que les SP n'entrent pas en action mutuelle avec le liant calcaire, cette action a un caractère d'adsorption qui provoque la désagrégation de particules calcaires hydratées. Ce processus s'accompagne d'une augmentation de volume du milieu dispersé ce qui, d'une part, conduit à l'accroissement de la mobilité des particules calcaires dans la solution et, d'autre part, à l'obtention d'une structure plus dense d'un composé calcaire durci donné. La structure plus dense et moins défectueuse du composé calcaire durci assure de plus hautes performances d'utilisation.

Le tableau 1 réunit les caractéristiques des composés d'injection élaborés par comparaison à celles des composés purement caséino-calcaires. Comme le démontre le tableau 1, tous les composés élaborés ont un avantage considérable sur les composés purement calcaires. La résistance à la compression plus élevée des composés caséino-calcaires s'explique par le fait que la pellicule de caséine en se disposant entre les agrégats structuraux d'un liant calcaire les fait coller en augmentant par ceci la résistance à la compression.

Tableau 1 Caractéristiques technologiques et physico-mécaniques des composés d'injection

N° d'ordre	Composition de la solution d'injection	Viscosité de départ MPa.s	Perte de volume %	Résistance à la compression MPa	Résistance adhésive MPa
1.	Solution calcaire	750-800	27-30	0,4-0,8	0,08-0,1
2.	Caséino-calcaire	1200-1250	18-19	4,4-4,8	0,14-0,16
3.	Pâte de chaux + CMO	700-750	9-11	2,4-2,6	0,8-0,2
4.	Pâte de chaux + SP-1	700-750	9-10	2,4-2,6	0,2-0,4
5.	Pâte de chaux + SP-2	200-250	8-9	2,2-2,4	0,2-0,4
6.	Pâte de chaux + SP-3	200-250	7-9	2,4-2,6	0,2-0,4
7.	Pâte de chaux + SP-2+CaCO ₃	600-650	2-3	2,8-3,6	0,5-0,7

Quant à la nécessité d'avoir des composés d'injection avec de hautes valeurs de résistance à la compression, c'est une question très problématique. Cette caractéristique, compte tenu du sens physique du processus de refixage par injection, ne joue pas un rôle tellement décisif comme la résistance adhésive, cette dernière étant considérablement supérieure dans les composés élaborés que dans les composés caséino-calcaires. La qualité et la solidité du refixage de l'enduit sur son support est fonction, en règle générale, du caractère stable des propriétés d'un composé injecté durant l'utilisation. Vu que la principale tâche d'un composé d'injection consiste à assurer une liaison faible de l'enduit avec son support, nous nous sommes fait un devoir d'estimer la variation de la valeur des résistances adhésives de composés d'injection durant le vieillissement artificiel.

Pour poursuivre les recherches on a préparé une série de pièces d'épreuve représentant des plaques de brique reliées avec divers composés d'injection. Après 28 jours de maintien à l'air en vue de leur durcissement on mettait les pièces d'épreuve dans une chambre climatique pour les soumettre à l'essai de température et d'humidité alternée cyclique.

Voilà le régime d'un cycle d'action climatique:

1. La température est égale à -30 °C, le maintien constitue 6 heures.
2. La température est égale à +15 °C, l'humidité relative est de 60%, le maintien constitue 6 heures.
3. La vitesse de variation de température est de 2°/min.

Après tous les 10 cycles d'essai climatique on faisait des mesures de la grandeur de résistances adhésives. Les résultats des essais ont montré qu'avec l'augmentation du nombre de cycles de vieillissement artificiel la grandeur de la résistance adhésive des composés d'injection diminuait. A noter qu'à une même durée de vieillissement les composés élaborés ont un avantage sur les composés caséino-calcaires. Les résultats des recherches ont démontré que les composés caséino-calcaires se détruisaient à peu près après 70 cycles de vieillissement tandis que les composés avec CMO et SP-1, après 100 cycles. Une attention particulière doit être portée aux composés avec SP-2 et SP-3 remplis de charges; lesdits composés gardent la résistance adhésive dont la valeur est un peu supérieure à la valeur de résistance adhésive de départ du composé caséino-calcaire, c'est-à-dire la valeur qu'on a avant de procéder au processus de vieillissement artificiel.

Conclusion

Ainsi, on peut conclure que les composés remplis de charges qu'on prépare à base de pâte de chaux et des SP diffèrent par leurs bonnes propriétés technologiques, à savoir une basse viscosité de départ, une perte insignifiante de volume durant le durcissement; une liaison fiable et durable de l'enduit avec son support est garantie. En comparant les processus technologiques lors du refixage des enduits au moyen du composé caséino-calcaire et des composés avec des SP on a conclu qu'il serait plus avantageux et économiquement plus efficace d'utiliser les composés élaborés.

Les composés d'injection avec des SP ont été testés lors des travaux de restauration pratique effectués à l'église de Saint-Jean-le-Théologien, à l'église d'Isidor (Rostov Vélikii), par le groupement "Rosrestavratsia", lors des travaux effectués en commun par des spécialistes soviétiques et bulgares à l'église de Saint Dimitri (village Arbanassi à la R.P.B.). Des conclusions positives et des procès-verbaux d'application sont faits à l'appui.

Pour conclure on tient à souligner que l'amélioration de la qualité et de durabilité des travaux de restauration n'est possible qu'avec une optimisation préalable des composés utilisés dans la restauration. Aussi l'étude des processus de vieillissement de matériaux et la mise au point dans des conditions de laboratoire des technologies d'application sont-elles obligatoires. Exclure absolument de la pratique de restauration des évaluations subjectives de la qualité, utiliser des méthodes accessibles au contrôle quantitatif des principales exigences technologiques auxquelles doivent satisfaire les matériaux de restauration permet d'une part d'élargir, avec des arguments scientifiques bien motivés, l'assortiment desdits matériaux, et d'autre part, de garantir une bonne qualité de travaux de restauration réalisés et leur caractère durable pendant l'utilisation d'un monument restauré.

Bibliographie

1. Briaguine, D.E. Essais sur le renforcement des supports de mortier des peintures murales anciennes à l'aide des solutions caséino-calcaires. - Etude et restauration des monuments culturels., M. 1982, P. 200
2. Kasparov, S.G. Kisliakovskaya I. N. Etude sur le mécanisme d'action des caséines dans les composés d'injection par le test calciare., Expressinformatsiya VNIIR, Ed.8, 1986.
3. Kasparaov S.G., Nikonova N.S. - Elaboration des compositions d'injection à la base des liants calcaires. Expressinformationtsiya VNIIR, Ed.8, 1986
4. Kasparov S.G. Kolbassov V.M. - Etudes sur l'efficacité d'utilisation des superplastificateurs dans des compositions d'injection à la base des liants calcaires., Matériaux de construction, N° 4, M., 1988.

ABRÉGÉ

Cette étude présente la conservation et les interventions en restauration de la tombe de Néfertari et de ses peintures murales. Elle débute sur l'histoire de la documentation graphique de la tombe, la meilleure de toute la vallée, qui a permis une évaluation exacte des dégradations souffertes. Elle décrit les procédés de nettoyage, de consolidation d'urgence et les traitements définitifs, ainsi que la difficile élimination des restaurations antérieures. Le travail est complété par les analyses chimiques qui montrent l'utilisation de la gomme arabique comme liant, l'HUNTITE comme pigment blanc et le blanc d'oeuf comme vernis.

MOTS CLES

Néfertari, gomme arabique, huntite, jaune d'oeuf, documentation, Schiaparelli, préparation, plâtre, consolidation, tempera.

CONSERVATION ET RESTAURATION DE LA TOMBE DE NÉFERTARI DANS LA VALLEE DES REINES

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Introduction

La tombe de Néfertari, épouse préférée de Ramsès II, est creusée dans la roche du West Bank du Nil, dans la localité de Louxor, en Haute Egypte. La roche est d'origine calcaire, peu consolidée, avec d'importantes intrusions et de grandes fissures remplies de cristaux de sulfate de calcium. Dans toute la matrice de la roche se trouvent de grandes quantités de sels (chlorures de sodium) qui ont cristallisé secondairement sur la superficie des peintures ou juste sous la couche picturale, et ici réside la principale difficulté dans la conservation des peintures de cette tombe.

La tombe est creusée en deux niveaux principaux unis par un escalier de quatorze marches, et c'est au niveau inférieur que se trouve la chambre sépulcrale. Cette tombe fut autrefois entièrement pillée, et les quelques objets découverts à l'intérieur sont actuellement exposés au Musée Egyptien de Turin.

Les peintures recouvrent la totalité des murs et du plafond de la tombe. Les couleurs utilisées furent du blanc, du noir, du bleu, du rouge et du rose, du vert et du jaune. Leur composition est celle classiquement trouvée dans ce genre de pigments et aucune différence n'est à signaler avec ceux utilisés pendant le Nouvel Empire.

Histoire de la Documentation Graphique de la Tombe et des Peintures

La tombe fut découverte en 1904 par une expédition dirigée par Ernesto Schiaparelli et financée par le Musée de Turin. Pendant plus de vingt ans, cette expédition réalisa la plus complète documentation graphique en blanc et noir jamais réalisée jusqu'alors pour une tombe égyptienne. Plus de 250 photos furent prises, d'une qualité exceptionnelle et couvrant tous les coins et angles de la tombe. Ce travail nous offre des informations précieuses sur l'état de conservation des peintures d'autant plus que la qualité photographique des prises permet une comparaison exacte des compositions et des formes. Cette documentation photographique ne finit pas avec l'expédition italienne vu qu'en 1913, 1919, 1931, 1941, 1956, 1967, et actuellement, des prises photographiques continuent d'être réalisées, nous fournissant ainsi une séquence exceptionnelle de la vie de ces peintures.

A partir des photos prises et après une étude comparative exhaustive, nous remarquons que les dégradations les plus importantes aussi bien depuis l'époque pharaonique que jusqu'à celle que couvre notre information et qui débute en 1904, se produisirent dans le mur nord de la chambre funéraire et dans les murs adjacents, c'est-à-dire dans la petite chapelle du mur nord et dans les murs est et ouest les plus proches. Les dégradations sont produites par l'effet, parmi d'autres, de la recristallisation du chlorure de sodium, et d'importantes dégradations sont localisées également dans l'antichambre de la tombe et dans la partie droite de l'escalier qui unit la chambre funéraire et les pièces supérieures. Nous avons remarqué qu'à peu près la moitié des dégradations se sont produites à partir de la découverte jusqu'à nos jours. Les causes en sont pour une grande partie de vieilles et malheureuses restaurations, notamment celles réalisées en 1940, 1956, 1973 pendant lesquelles fut utilisée une grande quantité de plâtre et de ciment en guise d'éléments consolidants, ainsi qu'une importante quantité d'eau comme fluidifiant. Ces peintures sont extrêmement sensibles à l'eau, soit à cause de leur réalisation avec la gomme arabique ou à cause de la recristallisation des sels dans toute la superficie picturale.

Les pièces supérieures paraissaient être en bon état de conservation, mais leur examen en lumière ultraviolette révéla de grandes zones de repeints. La salle des vaches, celle en plus mauvais état, présente des repeints qui recouvrent de grandes zones perdues de la composition. Ces repeints se retrouvent dans les salles adjacentes et nous calculons une perte de peinture originale de plus de 25%.

Documentation et Traitements D'Urgence

En 1986, un accord fut signé entre l'Egyptian Antiquities Organization et le Getty Conservation Institute pour la conservation de la tombe de Néfertari. Vu l'état de conservation précaire et dangereux des peintures de la tombe, le travail débuta par un traitement de consolidation d'urgence, afin d'éviter de plus grandes pertes de peinture pendant la restauration de la tombe. C'est au mois d'avril de la même année, après les analyses géologiques, hydrogéologiques, biologiques, de mesures de couleur, et les analyses des échantillons de peintures, que débuta la consolidation d'urgence.

Préalablement, d'octobre à décembre 1986, l'équipe de restaurateurs dirigée par Paolo et Laura Mora avait réalisé la documentation de l'état de conservation de toute la tombe et des peintures, en considérant, parmi les facteurs, les conditions du support, les altérations des couches picturales, la typologie et le repérage des substances étrangères et les interventions réalisées antérieurement. (Signalons ici qu'il existe des interventions réalisées pendant l'époque pharaonique.) Un exemple de documentation du support sera donné dans lequel les points suivants ont été considérés: les fentes et les fissures, l'extrusion de certaines parties de la roche, la séparation des couches de préparation, le manque de cohésion de l'enduit, les lacunes profondes et les lacunes superficielles.

En ce qui concerne la documentation totale de la tombe, des photos de celle-ci ont été prises en blanc et noir et à l'échelle 1:10; sur chaque copie un papier transparent en acétate a été superposé sur lequel ont été dessinés tous les défauts, les manques, les interventions, etc...

La consolidation d'urgence a suivi aussitôt la documentation terminée; elle se réalisa au cours du printemps 1987. Le but en était la prévention, et le maintien de la tombe dans son état actuel, tout en prévenant d'éventuels et futurs endommagements, et fournissant le temps nécessaire au choix des systèmes, méthodes et matériaux de la restauration définitive. Les problèmes les plus importants qu'il fallait éviter avec ce système étaient la fragmentation et la dégradation des couches de l'enduit.

Vu la cohésion précaire des couches de préparation on choisit une méthode de consolidation provisoire qui ne supposait pas la consolidation complète de toutes les surfaces, mais qui pouvait permettre le travail de plusieurs équipes de restaurateurs en même temps.

De petites bandes de papier japonais furent utilisées comme éléments de soutien et l'adhésif choisi fut le Paraloid B72 dissous à 20% dans du toluène. Le choix de cet adhésif fut déterminé par de nombreux essais qui déconseillèrent l'utilisation d'une colle aqueuse quelconque, quelle que soit sa forme, vu la grande sensibilité des peintures à l'eau. En ce qui concerne le plafond et vu la loi de la gravité, les bandes de papier furent substituées par des bandes de gaze en coton de la même forme et de mêmes dimensions, nous procurant ainsi une force et une résistance majeures. Plus de 10.000 bandes de ces deux matériaux furent utilisées.

Méthode de Restauration

La première campagne de restauration systématique de la tombe de Néfertari débuta pendant les premiers mois de 1988; il y eut deux campagnes au cours de la même année.

Les interventions réalisées pendant les deux campagnes de 1988 portèrent sur le nettoyage, la consolidation et le traitement définitif aussi bien de l'enduit que des couches picturales, et furent centrées dans les zones de la chambre funéraire, celle-ci étant la plus profonde, la plus endommagée et celle qui avait subi le plus d'interventions abusives. La consolidation de l'enduit et des couches de préparation se réalisa moyennant l'injection ou pénétration d'un mélange adhésif composé de plâtre, sable et quelques gouttes de Primal AC 33. En ce qui concerne le nettoyage des peintures, on utilisa un jet d'air à très basse pression et une application localisée et contrôlée d'un solvant, (thinner).

L'un des problèmes supplémentaires que nous reconstrûmes fut celui de retirer les tissus protectifs qui avaient été placés sur de grandes superficies de la couche picturale. Ces tissus avaient été mis comme mesure de sécurité vers 1978. C'était des tissus

très épais, lourds et imprégnés d'une grosse couche d'acétate de polyvinyl. Plusieurs applications d'acétone et de thinner furent nécessaires pour arriver à dissoudre et retirer les tissus. Une autre intervention ancienne qui posa certaines difficultés fut celle de consolidation de la couche picturale réalisée par de petites bandes de tissu épais unies avec de la cire d'abeille. Il s'avéra extrêmement difficile de retirer ces tissus car la cire avait pénétré en profondeur à l'intérieur des couches de préparation et avait durci; la solution fut la triéline. Au fur et à mesure que ces anciennes consolidations étaient retirées, il fallait consolider les zones qui restaient libres au moyen de Paraloid B 72 dissous dans du toluène.

La consolidation et l'adhésion des couches de préparation à leur support en roche était primordial pour la survie des peintures et ce fut donc notre préoccupation majeure. Une fois terminées les zones où il y avait séparation entre l'enduit et le support, on procéda à la consolidation au moyen d'un mortier fluide ayant presque le même composition que l'enduit pharaonique. Le consolidant injecté se composait de trois parties de sable local préalablement lavé et d'une partie de plâtre; à ce mélange étaient ajoutées quelques gouttes de Primal AC 33. Dans certains cas, afin d'endurcir certaines couches de préparation très minces, on utilisa des résines acryliques en dissolution ou en émulsion avant l'application du consolidant.

Analyse de Matériaux

Alors qu'étaient réalisés les traitements de conservation et utilisant les minuscules fragments que nous obtenions, nous commençâmes à effectuer les analyses des matériaux constitutifs des peintures. Il n'y a pas eu d'analyse des pigments car ils ont déjà fait l'objet de bien des publications, certaines très récentes et bien documentées.

L'un des premiers problèmes à résoudre était celui de l'identification du liant utilisé; nous savions seulement qu'il était très soluble à l'eau. D'après les premiers résultats obtenus, il s'agissait d'un polysaccharide, et par l'analyse de chromatographie liquide, chromatographie en couche fine, puis chromatographie gazeuse avec détecteur de spectromètre de masses, nous vérifiâmes qu'il s'agissait sans aucun doute de gomme arabique locale. Elle était d'une typologie spéciale à laquelle il manquait la ramnose comme l'un des sucres, car elle avait la composition habituelle de l'acide glucoronique, arabinose, et galactose, exception faite de la ramnose déjà mentionnée. Toutes les analyses de références de gommes arabiques montrèrent la présence des quatre sucres cités et chacun d'eux contenait de la ramnose; des gommes arabiques provenant du Soudan, du Sénégal, et celles commerciales ont été examinées.

Dans le temple Ramaseum du West Bank, nous avons trouvé un arbre du genre Acacia avec de nombreuses exsudations de gomme et des échantillons ont été pris bien que ce ne fût pas la meilleure époque, les vraies exsudations se produisant en été. A partir de l'analyse de cette gomme nous avons pu prouver qu'il lui manquait également la ramnose ayant les mêmes proportions que la gomme des trois autres sucres.

Au niveau des analyses il fallait également résoudre la détermination d'un vernis original qui se trouvait sur les couleurs rouges et jaunes, à plusieurs endroits des peintures. Il s'agissait d'une protéine, et une fois réalisée l'analyse des aminoacides par chromatographie liquide d'interchange ionique, sur certaines parties des couleurs afin de leur donner un certain brillant ou une augmentation de la coloration.

Les études de sédiments et de composition du crépi de la tombe ont donné les résultats suivants: la pierre extraite de la tombe a été utilisée pour fabriquer la base du crépi formé de fragments de calcite broyée; puis des terres de différente granulométrie procédant des alentours de la tombe ont été ajoutées, et du plâtre à 5% a servi d'élément consolidant. La composition du crépi utilisé pour le plafond a été modifiée: 50% de plâtre en plus a été ajouté, ainsi que de la paille de blé comme élément de cohésion.

Les analyses réalisées sur les couleurs blanches des peintures de la tombe ont révélé que, pendant le Nouvel Empire, les égyptiens utilisaient comme pigment blanc un minéral rare nommé HUNTITE, qui est un double carbonate de calcium et de magnésium. Cette information est publiée pour la première fois en ce qui concerne la tombe de Néfertari, car ce minéral n'a été décrit qu'en 1953. De nouvelles analyses ont été réalisées sur

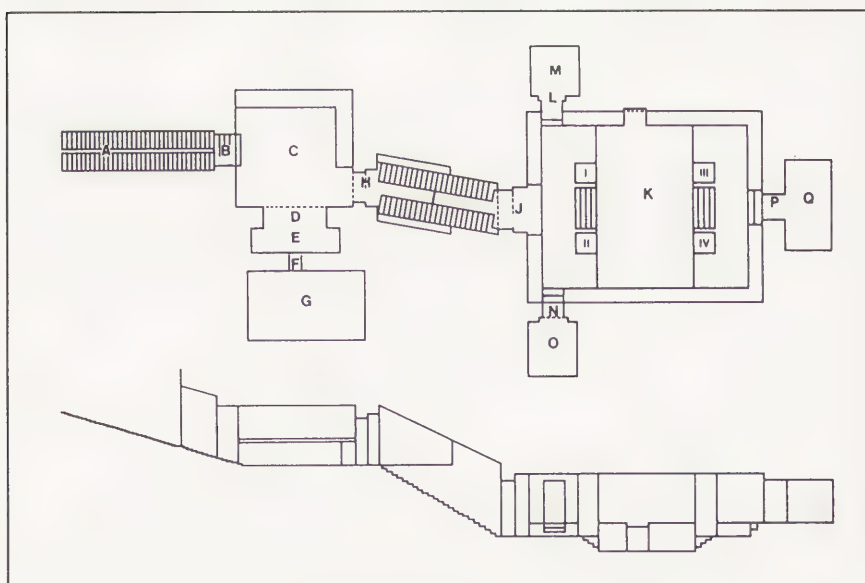
des peintures de la même époque pour vérifier si effectivement l'utilisation de l'huntite comme pigment blanc persiste. Les résultats des analyses confirment la présence d'huntite dans tous les pigments blancs. De plus l'intonaco de toute la tombe (la dernière couche blanche de préparation) est aussi de l'huntite. Il s'agit là aussi d'une nouvelle découverte.

Climat et Conservation

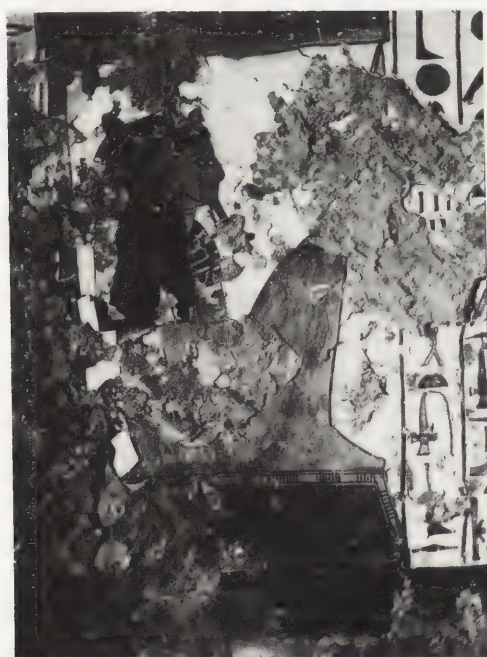
Les conditions climatiques à l'intérieur de la tombe de Néfertari sont très régulières tout au long de l'année. La température moyenne est de 30 C et l'humidité relative est de 30%. Cette petite quantité d'eau dans l'atmosphère a favorisé la conservation des peintures dans leur état actuel empêchant leur dégradation. Le volume de la tombe étant très réduit (la chambre funéraire a 250 m³), les moindres apports extérieurs de chaleur ou de vapeur d'eau modifient rapidement les conditions climatiques à l'intérieur. La présence de quatre personnes pendant une heure dans la chambre funéraire fait augmenter l'humidité relative de plus de 10 points et en même temps la température augmente d'un degré et demi. De plus, la récupération des conditions normales du climat est un procédé lent, étant donné que la tombe a un pouvoir d'auto-dépuration très limité et il faut un laps de temps assez long (plus de deux jours), pour retourner aux conditions climatiques antérieures lorsque les modifications introduites artificiellement ont été régulières.

Remerciements

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PLAN DE LA TOMBE



RÉSUMÉ

L'observation de quelques absorbants (CMC, pâte de cellulose, silice micronisée, kaolin) montre que leur capacité de rétention en surface de l'action des produits nettoyants varie énormément. Nous avons aussi observé d'autres paramètres importants pour le restaurateur comme la rétraction au séchage, la facilité de préparation, d'application et d'enlèvement, la toxicité, la coût.

MOTS-CLÉS

absorbant, fresque, carboxyméthyl-cellulose, kaolin, pâte de cellulose, silice micronisée

UTILISATION DES ABSORBANTS POUR LE NETTOYAGE DES FRESQUES

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1. Introduction

Lors du stage pratique avec un groupe d'étudiants du cours de Conservation des peintures murales de l'ICCROM, en 1988, nous avons utilisé plusieurs matériaux absorbants* pour maintenir en surface l'action des produits nettoyants. Au Château Caetani, à Sermoneta, nous avons commencé une expérience pour étudier l'efficacité de ces compresses.

Les absorbants sont utilisés dans plusieurs domaines de la conservation, par exemple pour le nettoyage des pierres, des papiers et des textiles; ils peuvent être utilisés avec des solvants aqueux ou organiques. Richard Wolbers a récemment étudié l'usage d'un type particulier d'absorbant, les gels, pour le nettoyage des peintures de chevalet [1]. En restauration des peintures murales, certains facteurs particuliers sont à considérer dans le choix des absorbants, étant donné les grandes surfaces à couvrir et la nécessité de travailler à la verticale ou sur des plafonds.

Le plus simple et probablement le premier produit utilisé en compresse fut le papier japon qui maintient l'action du solvant en surface pour un temps assez limité; le coton hydrophile (ouate) est aussi utilisé. Des argiles, comme la terre de Foulon, la terre de Sommières, la sépiolite et l'attapulgitite sont souvent mentionnées dans la littérature.

A Sermoneta, nous avons à notre disposition plusieurs absorbants: la carboxyméthyl-cellulose (un gel), le kaolin (une argile), de la pâte de cellulose et de la silice micronisée; nous avons tenté, avec des moyens assez élémentaires de comparer ces produits et leur capacité de maintenir en surface le plus possible l'action des produits nettoyants. Il est, en effet, souhaitable d'éviter la pénétration en profondeur de l'humidité qui peut dissoudre les sels solubles contenus dans le mur et les faire migrer en surface. Nous avons pu aussi comparer la rétraction des produits au séchage, paramètre important pour éviter les tensions sur la couche picturale. A cause du manque d'équipement, nous n'avons pu mesurer l'égalité du mouillage permettant d'éviter les discontinuités qui privent certaines parties de la surface de l'action du produit nettoyant, rendant ainsi irrégulier le nettoyage et obligeant à de nouvelles applications ponctuelles.

2. Méthodologie

Faute d'appareils de mesure sophistiqués sur le chantier, nous avons dû utiliser des moyens assez rudimentaires. Ce travail est donc très empirique et n'a d'autre but que de comparer entre eux l'action de quelques produits. Nous pensons que la simplicité de ces quelques tests est aussi un des aspects intéressants de l'expérience; les restaurateurs intéressés pourront refaire ces tests avec d'autres produits.

* L'usage n'a pas encore fixé un terme unique pour désigner les produits servant à maintenir en surface l'action des solvants; on retrouve dans la littérature les termes suivants: "absorbant", "compresse", "cataplasme", "pâte absorbante".

En anglais, on a aussi plusieurs variations: "absorbent", "compress", "poultice"; il semble cependant que ce dernier terme soit le plus approprié.

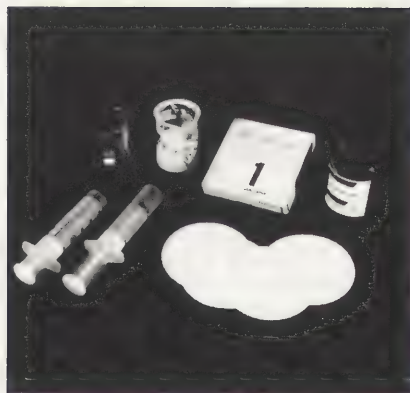


Fig.1 Institut canadien de conservation: reprise de l'expérience faite à Sermonetta (papier Whatman, bleu de méthylène, seringues tronquées pour l'application des absorbants)

L'expérience de chantier nous enseigne que la consistance requise pour tenir la compresse sur un mur vertical est obtenue en mélangeant les quantités suivantes de solide et de liquide pour les produits étudiés:

<u>Produits</u>	<u>Proportion de solide/liquide (en volume)</u>
CMC	2:10
Pâte de cellulose	20:10
Silice micronisée	15:10
Kaolin	25:10

Tableau 1



Fig.2 Illustration des différents absorbants: CMC, pâte de cellulose, silice micronisée, kaolin

Nous avons utilisé comme liquide**, une eau colorée afin de pouvoir contrôler visuellement la profondeur de pénétration du liquide. Des feuilles de papier essuie-mains nous ont servi de surface d'application; ce dernier choix est, en fait, à l'origine de l'expérience puisque nous avons constaté qu'un excédent de CMC laissé sur une feuille de papier essuie-mains n'avait pas même traversé cette surface. Ce matériel nous a permis d'observer facilement la pénétration du liquide dans une surface beaucoup plus absorbante qu'un mur (malgré leur nature et leur porosité différente, ces deux surfaces sont cependant hydrophiles). Nous avons donc superposé dix feuilles de papier essuie-mains sur lesquelles nous avons appliqué nos compresses colorées; la pénétration du liquide coloré pouvait être facilement contrôlée en calculant le nombre de feuilles traversées par le liquide dans un temps déterminé: 5 min., 15 min., 24h., 72 h. Ce matériel de fortune nous a permis aussi de constater un phénomène qu'une surface d'application rigide ne nous aurait peut-être pas permis de voir aussi facilement, c'est-à-dire les tensions que les matériaux constituant les compresses peuvent provoquer en séchant sur les surfaces où elles sont appliquées. (N.B. Les compresses n'ont pas été recouvertes, comme il est d'usage, d'une pellicule plastique mais laissées à l'air libre; ceci nous a permis de constater plus rapidement les tensions qui se créent lors du séchage.)

3. Observations

3.1 Nature chimique des absorbants

Il existe une différence chimique fondamentale entre la CMC et les autres absorbants que nous avons observés: la CMC [2] est un gel visqueux et homogène alors que les autres matériaux ne sont pas visqueux et leur phase liquide/solide reste distincte. Cette différence de nature explique l'excellente capacité de rétention de l'eau de la CMC et la grande quantité d'eau nécessaire à sa préparation.

3.2 Quantité d'eau nécessaire à la préparation

La première constatation a été la différence de quantité de liquide requise par chaque matériau pour obtenir la consistance désirée c'est-à-dire une pâte assez dense qui peut rester sur une surface verticale quand on l'applique en compresse plus ou moins épaisse (voir le Tableau I). La CMC s'est tout de suite différenciée des autres absorbants par la grande quantité d'eau qu'elle requiert, soit cinq fois le volume du solide. La quantité d'eau requise pour la pâte de cellulose varie selon le type de pâte utilisé: plus la fibre est longue, plus elle absorbe de liquide; il semble qu'il faille au moins de 50 à 60% de liquide pour que la pâte adhère au mur et cette adhésion demeure relativement limitée (voir 3.4).

** Le nettoyage des fresques s'effectue presque toujours avec des produits en solution aqueuse; nous avons donc fait nos expériences avec de l'eau colorée mais nous n'avons pas ajouté de produits nettoyants à cette eau. Nous savons que l'AB-57 contient un détergent qui modifie la tension superficielle de l'eau mais nous ne pensons pas que l'adjonction des autres sels utilisés pour le nettoyage aurait beaucoup modifié les propriétés que nous voulions vérifier. Les produits nettoyants utilisés à Sermoneta étaient le carbonate d'ammonium, le bicarbonate d'ammonium, le bicarbonate de sodium et l'AB-57.

3.3 Facilité de préparation et d'application

Tous ces produits sont faciles à préparer: il suffit de les mélanger avec le produit nettoyant (voir note au bas de la page 2). Les temps d'absorption du liquide varient cependant selon les matériaux. La CMC, la pâte de cellulose et le kaolin devraient préférablement être préparés à l'avance pour leur donner le temps de bien absorber le liquide. Il semble que pour la pâte de cellulose très fine, il soit même préférable de la préparer la veille pour le lendemain (cf: Sabino Giovannoni).

L'utilisation d'un mixer facilite le mélange homogène du solide et du liquide.

Pour la CMC, il est préférable de verser en pluie le solide dans le liquide; la CMC devient translucide après avoir absorbé l'eau.

Le temps nécessaire à l'application de la compresse varie selon la nature de l'absorbant choisi et la possibilité de l'appliquer ou non au pinceau, à la spatule, ou à la main; si le temps de contact nécessaire au nettoyage est bref, le restaurateur jugera, selon les cas, s'il est préférable ou non d'utiliser une compresse.

3.4 Mouillabilité, contact

Il y a un contact étroit entre le mur et les compresses de CMC, de silice micronisée et de kaolin.

La pâte de cellulose, par contre, adhère mal au mur et elle est incapable de retenir uniformément le liquide en surface; la pâte s'assèche rapidement en laissant fuir le liquide à la fois dans le corps poreux et dans la partie basse de la compresse où le liquide se concentre par gravité; ceci provoque des irrégularités de nettoyage et oblige à un remouillage de la compresse. Les possibilités de la pâte de cellulose peuvent cependant être améliorées grâce aux mélanges (Voir 4.1).

Selon le type de compresse choisi, l'utilisation d'un papier japon entre le mur et l'absorbant peut améliorer la qualité du mouillage; on doit utiliser un papier très fin qui se conforme aux irrégularités de la surface; certains utilisent aussi parfois, à cet effet, un non-tissé. (Voir 3.6).

La qualité du mouillage dépend beaucoup de la présence ou non d'un agent tensio-actif (détergent) dans le solvant utilisé, particulièrement avec des solutions aqueuses étant donné la forte polarité de l'eau. A Sermoneta, un seul des produits nettoyants utilisés, l'AB-57 [3], contenait un tensio-actif (Desogen^R). Vu la forte tension superficielle de l'eau, il serait sans doute préférable d'introduire un tel produit dans tous les mélanges à base d'eau utilisés pour le nettoyage des fresques.

3.5 Absorption, pénétration

La capacité de rétention du liquide par la compresse est évidente dès l'application. La CMC retient totalement le liquide tandis qu'un halo humide se forme immédiatement autour de la pâte de cellulose, de la silice micronisée et du kaolin. Cette migration de l'eau dans le mur peut entraîner la formation d'auréoles en surface; pour pallier à cet inconvénient, certains appliquent une "bordure" de pâte de cellulose à peine humide sur le pourtour la surface à nettoyer, ce qui limite la progression du halo (cf Sabino Giovannoni).

La pénétration dans l'épaisseur des feuilles de papier est tout aussi rapide et évidente. Le liquide de la CMC traverse à peine la première feuille, celui de la pâte de cellulose et de la silice micronisée baigne rapidement les dix feuilles superposées. Le kaolin retient le liquide dans les deux ou trois premières feuilles du papier.

La présence de papier japon ne semble changer ni la pénétration en profondeur ni la dispersion en surface du liquide.

<u>Produit seul</u>	<u>Temps</u>
CMC	rien après un jour; aucune auréole
Pâte de cellulose	10 feuilles après 30 min.; grande auréole
Silice micronisée	5-6 feuilles après 30 min.; auréole moyenne
Kaolin	2 feuilles après 30 min.; petite auréole
<u>Mélange</u>	
CMC + pâte de cellulose 1:1	4 feuilles après 30 min.
CMC + pâte de cellulose 1:2	10 feuilles après 5 heures
CMC + silice	2 feuilles après 30 min. (?)
CMC + kaolin	2 feuilles après 30 min. (?)
Pâte de cellulose + kaolin	10 feuilles et grande auréole après 15 min.
Pâte de cellulose + silice	10 feuilles et petite auréole après 15 min.

Tableau 2: Absorption, pénétration

3.6 Facilité d'enlèvement

Les absorbants étudiés peuvent être utilisés directement sur la surface peinte mais il nous semble préférable de les appliquer sur une feuille de papier japon afin de permettre l'enlèvement de la compresse d'un seul coup et d'éviter la pénétration de l'absorbant dans les craquelures. Le papier japon laisse pénétrer le produit nettoyant mais non les particules solides de l'absorbant.

La CMC ayant des propriétés adhésives, on constatera, si on l'utilise directement sur le mur, qu'elle colle parfois trop bien à la surface. On conseille d'éliminer la plus grande partie de la compresse mécaniquement et de très bien rincer ensuite tous les résidus avec de l'eau. Même employée sur un papier japon, la CMC laissera sur le mur des résidus qu'il faudra rincer soigneusement après l'enlèvement de la compresse.

La pâte de cellulose est généralement facile à enlever (selon la finesse des fibres); elle peut être lavée et réutilisée. La silice micronisée et le kaolin sont des poudres très fines, qui peuvent s'infiltrer dans les craquelures et être très difficiles à enlever par la suite.

3.7 Rétraction au séchage

Lors des tests, à Sermoneta, nous n'avons pas recouvert les absorbants d'une pellicule de plastique afin de pouvoir constater plus rapidement les effets du séchage. Les résultats des expériences, confirmés par des restaurateurs, montrent qu'il peut être très dangereux de laisser sécher la compresse sur le mur; la traction exercée alors sur le mur pourrait même provoquer l'arrachement de la couche picturale.

L'absorbant le plus dangereux, à cet effet, est la CMC.

<u>Produits purs</u>	<u>Rétraction après séchage</u> (x= le meilleur)
CMC	xxxx
Pâte de cellulose	x
Silice micronisée	xxx
Kaolin	xx
<u>Mélanges 1:1</u>	
CMC + pâte de cellulose	xx
CMC + silice	xxxx
CMC + kaolin	xxxx
Pâte de cellulose + kaolin	xx

Tableau 3

3.8 Dangers pour la santé

Toute substance à l'état de poudre légère présente un danger pour les voies respiratoires. En cas d'inhalation, les particules de silice contenues dans les argiles (kaolin, attapulgite, sépiolite, terre de Foulon, terre de Sommières) peuvent irriter

les poumons et provoquer la silicose. Parmi les produits avec lesquels nous avons travaillé, la silice micronisée est, à l'état sec, celui qui présente le plus grand danger pour la santé puisqu'il s'agit de silice pure réduite en particules extrêmement fines et ultra-légères.

L'attapulгите est une argile absorbante qui est souvent mentionnée pour le nettoyage des pierres; elle est cancérogène [4].

3.9 Translucidité

Il est toujours prudent de pouvoir contrôler visuellement l'effet des produits utilisés pour le nettoyage. Malheureusement, la plupart des absorbants sont opaques et dissimulent donc, une fois appliqués, la surface que l'on veut nettoyer. Parmi les absorbants que nous avons observés seule la silice micronisée et la CMC offrent une certaine translucidité.

3.10 Coût

La CMC et le kaolin sont, en général, bon marché. Selon les pays, le coût de la pâte de cellulose peut varier mais elle est rarement chère; on peut aussi la réutiliser après lavage. Le coût de la silice micronisée peut, par contre, être prohibitif compte tenu des surfaces à couvrir.

4. Mélange de différents absorbants

Les possibilités de mélanges entre les différents absorbants sont nombreuses. On choisira un mélange selon les exigences de chaque travail, de la surface à nettoyer (lisse ou irrégulière), du temps de contact nécessaire, de la nécessité de garder l'action du produit nettoyant en surface, des disponibilités de matériel. Il est important cependant de bien connaître les propriétés des absorbants et les proportions dans lesquelles on peut les mélanger pour obtenir les caractéristiques désirées.

4.1 CMC et pâte de cellulose

On peut améliorer le contact de la pâte de cellulose et de la surface à nettoyer en mélangeant dans des proportions diverses la pâte de cellulose avec de la CMC (ex. 1:1, 1:2). La CMC perd cependant alors ses excellentes qualités de rétention de l'action du liquide en surface; si on dépasse la proportion 1:1, la pénétration du liquide dans le support est considérable. Il est à noter que la pâte de cellulose entraîne alors la colle dans le support comme le montrent les feuilles de notre échantillon numéro 6 (CMC et pâte de cellulose 1:2) qui étaient collées sur quatre épaisseurs.

4.2 CMC et silice micronisée

Ces deux absorbants ont une forte rétraction en séchant. La CMC donne cependant à la silice de meilleures qualités de rétention du liquide en surface (1:1). Ce mélange est translucide.

4.3 CMC et kaolin

La CMC améliore aussi la performance du kaolin pour la rétention en surface du liquide (1:1).

4.4 Pâte de cellulose et kaolin

La pâte de cellulose se rétracte davantage en séchant lorsqu'elle est mélangée au kaolin (1:1). Le kaolin ne semble pas pouvoir conférer à la pâte de cellulose une meilleure rétention du liquide en surface.

4.5 Pâte de cellulose et silice micronisée

On remplace parfois la CMC par la silice, plus facile à enlever. Selon Madame Laura Mora, il est cependant toujours préférable de mettre un peu de CMC dans le mélange pour retenir l'humidité en surface.

5. Conclusion

On ne peut pas toujours sur un chantier s'offrir le luxe de mesurer au gramme près la quantité des produits utilisés; il est cependant important de se rappeler qu'on ne peut mélanger dans n'importe quelle proportion les différents absorbants. Il faut garder à l'esprit les caractéristiques suivantes :

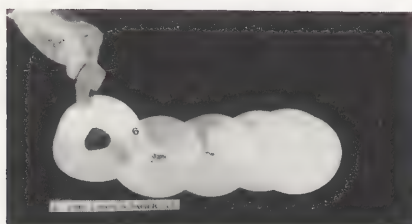


Fig.3 CMC et pâte de cellulose: adhérence des feuilles de papier suite à la migration de la CMC

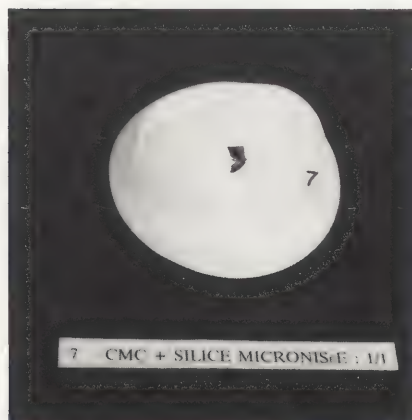


Fig.4 CMC et silice micronisée 1/1: rétraction au séchage

La CMC présente des qualités fort intéressantes pour le nettoyage des peintures murales; elle permet, en effet, de retenir parfaitement en surface l'action du produit nettoyant, paramètre important lorsqu'on veut éviter de déranger les sels solubles dans le mur. La très forte rétraction au séchage de la CMC rend cependant celle-ci potentiellement dangereuse si on néglige de la très bien rincer et qu'elle sèche sur la surface.

La pâte de cellulose ne retient aucunement le liquide en surface.

Un contact étroit de la compresse avec la surface à nettoyer est parfois indispensable; à notre avis, il serait cependant préférable, lorsque les résultats sont satisfaisants, d'utiliser les absorbants au travers d'un papier japon afin de faciliter l'enlèvement de la compresse et d'éviter la pénétration de particules dans les irrégularités du support. Les résidus d'absorbants rendent nécessaire de nombreux rinçages, ce qui augmente les risques d'abrasion de la couche picturale. Ces résidus, particulièrement ceux de la CMC, peuvent en outre exercer sur la surface peinte une forte action mécanique qui peut aller jusqu'à l'arrachage de la couche superficielle.

Les absorbants sont des auxiliaires précieux pour les restaurateurs puisqu'ils travaillent pour nous! S'ils sont employés judicieusement, ils permettent d'éviter les risques d'abrasion que peuvent causer les nettoyages et les rinçages répétés.

Remerciements

Nous avons beaucoup apprécié l'intérêt manifesté pour notre expérience par les participants et les professeurs du Cours de conservation des peintures murales, ICCROM 1988. Plusieurs personnes nous ont fait part de leur expérience au cours de cette recherche et nous tenons à les remercier ici chaleureusement. Nous sommes particulièrement reconnaissantes à Madame Laura S. Mora et à Monsieur Paul Mora qui nous ont encouragées à écrire cet article. Monsieur Scott Williams et Madame Carole Dignard, de l'Institut Canadien de Conservation, nous ont aussi donné de précieux conseils lorsque nous avons rédigé de cet article et refait les expériences en laboratoire; nous tenons à préciser que ces expériences ont corroboré nos essais à Sermoneta. Les photographies illustrant cet article ont été prises lors de la reprise des expériences à l'Institut canadien de conservation.

Bibliographie

1. WOLBERS, Richard C, Notes for Workshop on New Methods in the Cleaning of Paintings, The Getty Conservation Institute, August 15-26, 1988.
2. HERCULES, Cellulose Gum. Sodium Carboxymethyl Cellulose Gum. Chemical and Physical Properties, Wilmington (Delaware), 1980.
3. MORA, P. et L., et PHILIPPOT, P., La Conservation des peintures murales, Editrice Compositori, Bologne, 1977, p.335 et p.400-401 ("absorbants" et "compresses")
4. GROSS, Paul et Daniel C. BRAUN, Toxic and Biomedical Effects of Fibers, Noyes Publications, 1984, p.138-139.

ABSTRACT

For the first time in history investigations of old Russian wall painting discovered green copper pigments. Three of them: malachite, atacamite and poznyakite are artificial in origin, the fourth one is natural pseudomalachite. Poznyakite, hydrated copper sulphate, was identified for the first time in the history of investigating wall and easel painting. The synthesis of malachite, atacamite and poznyakite was carried out. The form and structure of the synthesized compounds and the pigments from a paint coating completely coincide.

KEYWORDS

Green copper pigments, wall painting, synthetic and natural minerals.

NEW DATA ON GREEN COPPER PIGMENTS IN WALL PAINTING

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Introduction

Investigations of painting, conducted over the past years in many countries, substantially expanded our knowledge of minerals used as pigments. There appeared new information on the use of artificial analogues of natural minerals, whose synthesis must have been sufficiently well-known in the past.

Particularly interesting results were obtained when investigation green pigments. Beginning from the 70's, a number of papers have been published, presenting the results of identifying green copper combinations whose use in painting has been unknown before. The traditional set of green copper pigments, malachite, verdigris and copper resinate, has been considerably expanded by such substances as atacamite, paratacamite, pseudomalachite, gerhardite, calumetite, antlerite, chalconanthronite and langite.

Most of these compounds were used in paintings on Egyptian sarcophagi, in easel and miniature painting and in polychromatic sculpture. Green copper pigments were less often used in wall painting; there are papers on the use of malachite, calumetite, antlerite and paratacamite in wall painting on the 11-16th century West-European monuments.

Our investigations of wall paintings in Novgorod (12-17th centuries), Rostov Yaroslavsky (17th century), Vladimir (16th century), Moscow Kremlin Assumption Cathedral (15th century), a 13th century church in Akhtala (the Armenian SSR) and the Church of Nativity of Our Lady in the village of Arbanasi (Bulgaria, 17th century) failed to discover copper compounds in painting coatings.

A 16th century monument, the Nativity of Our Lady's Church in the Ferapontovsky Monastery, proved to be very surprising in the variety of copper compounds used.

We conducted investigations based on a complex of physico-chemical analysis methods: microscopic technique (in ordinary reflected and passing polarized light), microchemical qualitative analysis, emission spectral, roentgenophase analysis; in certain cases microroentgenospectral analysis and raster electron microscopy. These investigations showed that green colour takes a high place in painting on monuments. It is produced in a variety of ways.

Green clothes in a church dome, some clothes on walls and dome elements were painted with a mixture of azurite and yellow ochre. Practically the only green pigment in a chapel of St. Nicholas Church is glauconite, one of the most common pigments in easel and wall painting.

Alongside that, all green grounds and most of the clothes of saints on walls and pillars were painted with green copperbearing pigments, among which we identified: natural pseudomalachite, artificial malachite, poznyakite and atacamite.

Pseudomalachite is present in paint coatings in a finely ground state. This pigment has never been identified before in old Russian painting. It was discovered in 11-16th centuries manuscripts by foreign investigations.

Malachite was found in paint coatings in the form of rounded green particles with a radial ray structure and bright interference colouring, characteristic of carbonates; these particles are in the form of spherulites from several to 300-500 mcm in size. Calculations of these particles, made by means of roentgenophase analysis, coincide with those of malachite. However, prismatic and needle crystalline form is characteristic of natural malachite. Malachite, present in paint coatings by way of spherulites, led to a proposition that it was made artificially.

Along with artificial malachite, a large quantity of saccharoidal blue congestions of particles, were found consisting of very thin weak anisotropic plates, inside which there were spherulites. The size of spherulites ranges from micron shares to 3-5mcm.

Investigations by a raster electron microscope found that the plates had a fine-grain structure. Plate composition was ascertained by means of a microprobe: basic elements were Cu, Ca, admixtures were Fe, Mg, Al. Blue aggregates appear to be an intermediate stage in the formation of artificial malachite. Found in all paint coatings, containing artificial malachite, they can possibly be another proof of the artificial origin of malachite.

Poznyakite is present in paint coatings along with malachite by way of blue plates with grey interference colouring. These plates reach sometimes 1 mm in size. It can be clearly seen in crossed nicols that they consist of several fused monocrystals with different orientation and look like dicerseely dimming sectors. Sometimes these plates consisted of the finest spherulites seen at the limit of 400 - power resolution.

In addition to copper, sulphur was discovered in the crystal when investigating by an electron microscope with a microprobe attachment. A roentgenogram of blue crystals made it possible to ascertain the mineral definitively as hydrated copper sulphate, poznyakite. This mineral has never been identified in painting before.

Crystals of natural poznyakite and poznyakite from the paint coating have under microscope a laminated shape, but numerous joints of poznyakite crystals of the paint coating, forming different regular crystalline forms (stars, trihedrons, etc.) demonstrate that it is artificial in origin. It is obvious that raw material for making pigments was not a piece of mineral in the shape of a stone, subjected in such cases to a thorough fine grinding, as a result of which regular forms of individual crystals are, as a rule, destroyed, but ready-made finely dispersed powder was used instead. Obtained synthetically by precipitation from a solution, it did not require grinding and pulverization and, therefore, the form of individual particles in precipitation remained as it was.

Atacamite was identified in paint coatings along with artificial malachite. This mineral was found earlier by us in a 13th century manuscript, in a 17th century geographical map and in a 16th century icon.

Atacamite, found in paint coatings of the Ferapontovsky Monastery wall paintings, is characterized by a variety of crystal forms (plates, fusions in the shape of stars), which shows an artificial origin of this mineral. The artificial origin of atacamite and poznyakite is proved also by crystals with malachite spherulites fused into them, which is possible only in their joint precipitation.

The investigation results of the above-said Ferapontovsky Monastery wall paintings became a stimulus to work on synthesizing individual minerals, as well as mixtures characteristic of a paint coating: malachite with atacamite, and malachite with poznyakite. It was interesting to establish whether these pigments were synthesized separately and then mixed, or whether a mixture was obtained right away with the required green tone; what the shape of particles in synthetic precipitation was, and to what extent it was comparable to the shape of particles of similar compounds from a paint coating.

Poznyakite production. The experiments were based on the synthesis technique developed by G.O.Nechiporenko who was the first to make poznyakite artificially /1/.

Poznyakite was synthesized by adding NaHCO_3 powder to sulphuric acid copper solution. The optical properties and crystalline structure of artificial and natural poznyakite are identical, but their crystals have different morphological features, which can be seen quite well by means of 400-power microscopic observation of permanent preparations. When comparing permanent preparations of natural and synthetic minerals to permanent preparations from the paint coating of wall painting, one has to admit its proximity to synthetic samples.

Malachite was made by adding either NaHCO_3 powder or NaHCO_3 solution to the sulphuric acid solution. An emerald green precipitation occurred with the 3 correlation of concentrations of ion-bicarbonate to ion-sulphate. The precipitation was studied microscopically and roentgenographically and was identified as malachite $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$.

Unlike natural malachite, the synthetic one is in the form of spherulites.

Comparison of synthetic malachite to the malachite, found in paint coatings of wall paintings, demonstrates their similarity.

Having taken the technique of production of artificial poznyakite as a basis, we succeeded in making a mixture of poznyakite and malachite. By adding different amounts of NaHCO_3 , we obtained different values of initial $\text{pH} > 6$, to > 7 . Poznyakite was in the form of laminated pale blue crystals, complex doubles and triples of regular hexagonal form, and malachite was in the form of spherulites.

The technique, described in the book /2/, was used as a basis of synthesizing atacamite.

Salt was added in varying quantities to blue vitriol solution; the precipitation of atacamite began in alkali medium ($\text{pH}=8$) which was obtained by adding the required quantity of 1N NaOH.

NaCl was introduced while mixing to sulphuric copper solution for the purpose of joint precipitation of atacamite and malachite; pH was raised to 8 by means of NaOH, and then sodium bicarbonate was poured in. The resulting precipitation is a 2-component mixture: atacamite by way of green particles with weak anisotropy, and malachite by way of fine spherulites.

Conclusion

For the first time, while investigating old Russian monumental painting on an early 16th century monument, green copper pigments were discovered: pseudomalachite, malachite, atacamite and poznyakite. Poznyakite, as far as we know, was for the first time in world practice identified as a pigment*. A peculiar shape of malachite, atacamite and poznyakite crystals, their mutual position in a paint coating shows their artificial origin. The synthesis was made of each individual pigment, as well as of pigment mixtures, characteristic of paint coatings in Dionysius' wall paintings. The synthesized pigments and mixtures are identical to paint coating materials.

Bibliography

1. G.O.Nechiporenko. Proceedings of the USSR Mineralogical Society, Part 100, issue 6, 1971, pp. 754-756.
"On Synthetic Poznyakite".
2. L.P.Listova and A.A.Ryabinina. Geokhimiya, Moscow, 1971, pp. 1380-1388.
"Experimental Investigation of Precipitation of some Copper Compounds".

Table

Roentgenometric Data on Poznyakite $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$

ASTM, Canada (1968), 20-364		Poznyakite from paint coating ¹	
1/10	d	1/10	d
1	2	3	4
100	6.94	e.w., v.i.	6.90
8	5.25	-	-
4	5.15	-	-
6	4.85	-	-
4	4.77	-	-
2	3.74	-	-
30	3.47	i.	3.47
6	3.33	-	-
4	3.23	-	-
2	2.88	-	-
2	2.79	-	-
25	2.70	av.	2.71
16	2.614	-	-
2	2.576	-	-
25	2.42	av.	2.42
12	2.33	-	-
8	2.26	av.	2.25
12	2.018	av.	2.01
6	1.952	av.	1.964
4	1.870	av.	1.85

*Simultaneously, poznyakite was identified by us in green paint coatings of A.Bronzino's picture "The Holy Family" (from the Pushkin State Fine Arts Museum collection, Moscow).

1	2	3	4
2	1.734	w.	1.725
4	1.662	-	-
2	1.616	-	-
4	1.585	w.	1.595
10	1.541	w.	1.540

Relative intensity: v.i. - very intensive,
i. - intensive,
w. - weak,
av. - average,
e.w. - especially weak.

[†]The sample was X-rayed at the URS 2.0 instrument, Cu - radiation 1 = 18 ma, U = 35 kv.

RÉSUMÉ

Ce travail présente la découverte d'un nouveau pigment bleu dans la peinture murale romane du XII^{ème} siècle dans les Pyrénées, et la méthodologie analytique utilisée pour démontrer qu'il s'agit du minéral aérinite. Il contient également une étude comparative de plusieurs peintures murales conservées in situ ou dans les Musées de la région catalane où les bleus ont été réalisés avec ce minéral. Actuellement, un projet de recherche a débuté qui inclut toute la peinture murale médiévale des Pyrénées.

MOTS CLEFS;

Phyllosilicate, aérinite, pigment bleu, peintures murales romanes, Pyrénées.

LE BLEU AERINITE: UN PIGMENT MECONNU EN PEINTURE MURALE ROMANE.

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INTRODUCTION

Ce travail est né à partir de la recherche effectuée sur les couleurs utilisées par les artistes anonymes de l'art roman catalan. C'est le premier travail sur un nouveau pigment depuis cinquante ans, étant donné que tous les pigments en peinture murale ont déjà été décrits depuis longtemps.

Le travail présenté est une première étude sur ce minéral rare, et nous pensons que bien des bleus ont été, dans de nombreux pays, attribués par erreur à des glauconites ou autres pigments argileux alors qu'ils étaient de l'aérinite, et nous sommes convaincus que ce sera ainsi prouvé à partir de cette étude.

LA DECOUVERTE

Lors des études effectuées pour la conservation des peintures murales de l'église de La Cortinada dans la Principauté d'Andorre en 1986, nous remarquâmes que les bleus des peintures présentaient des caractéristiques chromatiques spéciales qui ne s'apparentaient à aucun des pigments utilisés jusqu'à présent dans nos peintures romanes catalanes et andorranes, et aucune référence bibliographique ne fut trouvée dans d'autres peintures.

Les premières analyses chimiques des échantillons de pigment bleu prélevés directement des couches picturales des peintures du XII^{ème} siècle de la Cortinada indiquèrent que la composition du pigment avait des caractéristiques matérielles propres, une chromaticité particulière, et que sa formule ne correspondait pas à celle des couleurs normalement utilisées dans l'art roman.

Grâce à la comparaison microscopique du pigment bleu avec des minéraux aux textures et couleurs semblables, nous arrivâmes à la conclusion qu'il s'agissait d'un minéral rare, aux tons bleu clair, appelé AERINITE et dont les principaux gisements se trouvent dans des zones localisées des Pyrénées.

DESCRIPTION DU MINERAL

Le minéral aérinite (qui en grec signifie bleu ciel) fut décrit pour la première fois en 1876 par A. Von Lassaulx, minéralogiste allemand fort connu, qui le baptisa alors qu'il étudiait dans le Musée de Breslau une série de minéraux appelés "vivianite d'Espagne".

Ce minéral présente une morphologie fibreuse, aux fibres longues et groupées en faisceaux avec des inclusions prismatiques de quartz et d'autres minéraux de la même famille. Son ton varie du bleu clair au bleu très foncé, il présente des veines étroites et compactes, avec de nombreuses inclusions de roches voisines. Il s'agit d'un phyllosilicate d'altération des ophites, d'origine hydrothermale que l'on trouve dans les zones triasiques.

En termes géologiques, ce minéral est difficilement classifiable, car on n'avait pu jusqu'à présent isoler le monocristal d'aérinite.

En 1942, Gettens et Stout décrivent pour la première fois ce minéral, en relation avec des matériaux picturaux, et le classifient dans le groupe des chlorites. En 1985, une étude de l'Université de Saragosse le classe comme appartenant au groupe des zéolithes, classification confirmée par la récente étude de l'Université de Toulouse.

DISTRIBUTION GEOGRAPHIQUE DU MINERAL ET DES PEINTURES

Le minéral aérinite se trouve principalement dans des zones proches des Pyrénées, dans la région de Huesca (Estopiñán del

Castillo, Juseu, Nacha, etc....), et de Lérida (Les Avellanes, Ager, Artesa de Segre, Hostalets de Tost). On le trouve également à Saint-Pendelon dans les Landes françaises, et selon des informations récentes, il existerait aussi dans le nord de l'Italie.

A partir des études effectuées dans divers ensembles de peintures murales d'origines diverses, nous avons obtenu les résultats suivants: les bleus de toutes les peintures murales romanes de la Principauté d'Andorre ont été réalisés avec ce pigment. Jusqu'à présent, un ensemble de 10 peintures a été localisé dans la Principauté.

En ce qui concerne la Catalogne et sa peinture murale, nous remarquerons que la peinture qui se trouve au Musée d'Art de Catalogne a été réalisée dans sa majeure partie avec l'utilisation d'aérinite. Pour être plus précis, les ensembles muraux les plus importants, celui de Sant Climent et de Santa Maria de Taull ont été exécutés avec ce pigment bleu. Bien que dans certains cas d'autres pigments aient été utilisés tels que l'azurite et le lapis-lazuli, l'aérinite est cependant le plus fréquent, et il peut apparaître dans une même peinture avec d'autres pigments bleus.

La proximité des gisements d'aérinite n'implique pas forcément son utilisation par les peintres médiévaux. Effectivement, dans la Colegiata de Ager, bien que le minéral aérinite soit à quelques mètres du monument, seul le lapis-lazuli a été utilisé comme pigment bleu.

ANALYSES ET RESULTATS

La première démarche dans le grand ensemble des analyses effectuées aussi bien sur les échantillons des peintures que sur le minéral a été de déterminer leur ressemblance morphologique et la localisation des gisements du minéral.

Les analyses réalisées sont les suivantes:

- **Analyse microscopique:** en lames minces par lumière transmise, nous observons que la morphologie et les paramètres optiques entre les échantillons des peintures et le minéral sont identiques. On constate un fort pléochroïsme, et avec les nicols croisés, les couleurs d'interférence sont d'une tonalité jaunemarron, avec un bas indice de réfraction, approximativement 1,5. Les tons des couleurs d'interférence varient du marron au rouge, en fonction de l'origine du minéral et des traitements thermiques appliqués sur celui-ci.

- **Diffraction des rayons X:** cette analyse indique une totale identité entre l'aérinite et les échantillons pris sur les peintures. Les paramètres cristallographiques les plus notables sont les suivants: 14,8068 Å., les plus intenses à 100%, 4,0528 Å, 3,7948 Å, 3,6495 Å, 3,4359 Å, 3,2100 Å, 2,9978 Å, 2,8100 Å, 2,7179 Å, 2,5687 Å, 2,5158 Å, 2,1331 Å, 1,7509 Å, 1,6228 Å.

- **La microfluorescence des rayons X** nous donne la composition chimique suivante de l'aérinite: SiO_2 45,21%, Al_2O_3 14,92%; CaO 11,09%; Fe_2O_3 total 8,93%; MnO 0,11%; P_2O_5 0,13%; TiO_2 0,62%; MgO 5,91%; K_2O 0,18%; perte par calcination 13,70%.

- **L'analyse volumétrique** a été effectuée afin de déterminer le rapport Fe^{2+} et Fe^{3+} en obtenant les résultats suivants:

- * Aérinite claire, $\text{Fe}^{2+}/\text{Fe}^{3+}$ 0,478
- * Aérinite foncée, $\text{Fe}^{2+}/\text{Fe}^{3+}$ 0,326

- **L'analyse thermogravimétrique** nous montre que le minéral perd du poids graduellement, sans bond significatif, jusqu'à atteindre la température de 1000° C. A partir de 300° C. on observe une perte de couleur importante en atmosphère inerte, alors que cette perte se produit à 250° C. en atmosphère oxydante. La perte complète de la couleur se produit entre 250° C. et 400° C., avec une perte d'eau de 2,75% et dans cette fourchette de températures le rapport $\text{Fe}^{2+}/\text{Fe}^{3+}$ diminue de 0,357 à 0,143.

- **La spectrophotométrie d'absorption en IR** nous indique la présence de petites quantités de carbonates, de silicates et d'eau de cristallisation.

Conclusion des résultats des analyses: il n'existe aucun doute, les pigments bleus prélevés et le minéral aérinite ont la même composition.

La couleur bleue est due au rapport $\text{Fe}^{2+}/\text{Fe}^{3+}$; plus ce rapport est élevé, c'est à dire plus grande est la proportion de Fe^{2+} et plus

intense sera la couleur. La présence dans l'aérinite d'eau de cristallisation associée au Fe^{2+} joue également un grand rôle dans sa coloration. Il s'agit d'une argile, d'un silicate d'aluminium et de calcium hydraté, d'altération ophitique.

TECHNIQUES DE FABRICATION

Afin que le minéral aérinite puisse être utilisé comme pigment en peinture murale, il doit être soumis à une série de traitements préliminaires, car ses impuretés naturelles empêchent son utilisation dans son état brut. Les morceaux les plus purs du minéral sont d'abord sélectionnés. Ils sont ensuite triturés de façon à obtenir des morceaux suffisamment grands pour permettre une première extraction des impuretés (ophites). Ces impuretés sont enlevées au fur et à mesure du broyage jusqu'à l'obtention de la poudre. Effectivement, si ces étapes n'étaient pas respectées pendant le broyage, la poudre obtenue perdrait le bleu intense initial.

La purification du minéral moulu s'effectue par décantation, et sa densité est de 2,13. Nous obtenons ainsi une purification partielle et un enrichissement du minéral par l'élimination des impuretés. Les décantations s'effectuent avec de l'eau, et le minéral est ensuite séché par évaporation naturelle.

AERINITE ET PROCÉDES PICTURAUX

Les différentes techniques picturales qui peuvent être utilisées avec le minéral aérinite sont la peinture à fresco, à la détrempe et à la chaux. Avec ces procédés nous obtenons des couleurs acceptables quant à leur brillance et leurs tons. Mais, pour ce qui est de la peinture à l'huile, nous obtenons une couleur bleu foncé qui permet difficilement le mélange avec d'autres couleurs.

BIBLIOGRAPHIE

LASSAULX A. Von (1876): "Aërit, ein neues Mineral". N.jb.Min., pg. 175 et 352-358.

CALDERON S. (1917): "Los minerales de España". Junta para la ampliación de estudios e investigaciones científicas. Madrid, tomo II, pg. 391-394.

TOMAS LLORENÇ: "Els minerals de Catalunya". Treballs de la Institució Catalana d'Història Natural. Barcelona. Instituts d'Estudis Catalans (1919-1920), pg. 170.

GARRIDO, J: "Sur l'aérinite". Bull.Soc.Fr.Min.Crist., (1949), pg. 401-407.

GETTENS, RUTHERFORD, STOUT: "Painting Materials". Dover Publications, (1942).

GALAN Y MIRETE: "Introducción a los minerales de España." IGME, pg. 420.

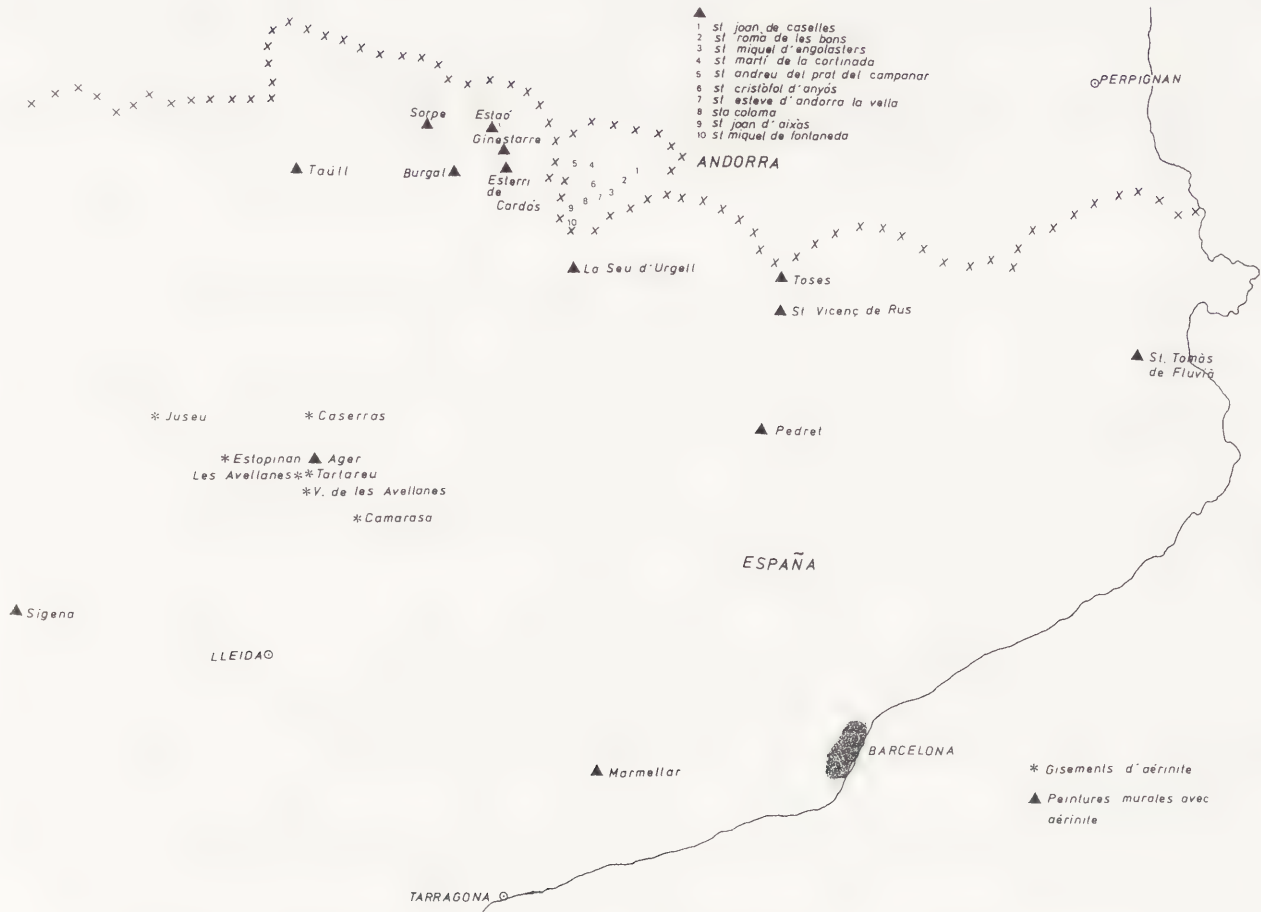
BESTEIRO, LAGO, POCIVI, BASTIDA, MOLINER: "Acta Geológica Hispánica, v.20 (1985), n. 3/4, pg.257-266.

AZAMBRE, MONCHOUX: Bull.Minéral. n.111, p. 39-47. (1988).

PALET CASAS, A.: "Tesis Doctoral". Nov. 1988. ISBN84-7528925-8.

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DISTRUBUTION GEOGRAPHIQUE DE L'AERINITE ET DES PEINTURES

Composition chimique de l'Aérinite.

	Claire (Estopiñan)	Foncée (Avellanes)	Roche mère
SiO ₂	45.21	46.91	49.73
Al ₂ O ₃	14.92	12.77	13.52
CaO	11.09	10.62	9.88
Fe ₂ O ₃ (total qui n'intervient pas dans la couleur).	6.33	7.09	9.49
FeO	0.76%	0.81%	-----
Fe ₂ O ₃	1.75%	2.72%	-----
Fe ₂ O ₃ (total associé à la couleur).	2.60%	3.62%	-----
MnO	0.11	0.09	0.15
P ₂ O ₅	0.13	0.10	0.08
TiO ₂	0.62	0.82	0.97
MgO	5.91	6.10	7.11
K ₂ O	0.18	0.37	0.64
H ₂ O (1000°C)	13.70	13.82	9.95
total	100.80	101.41	101.52

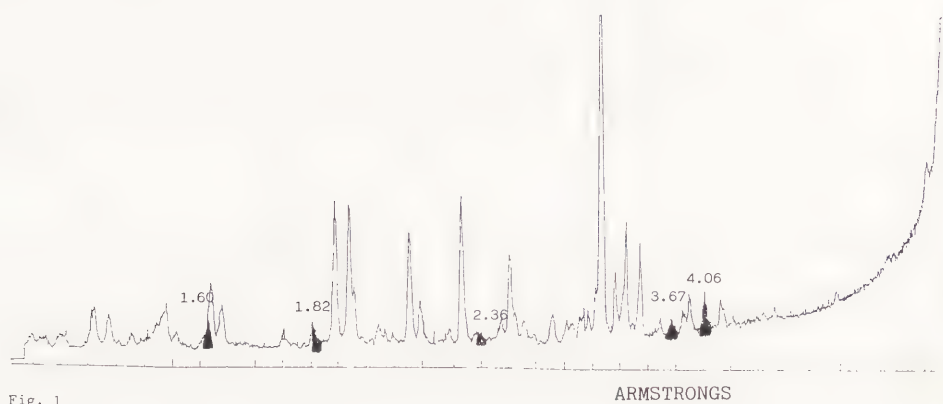


Fig. 1

DIFRACTOGRAMME DE RAYONS X D'UN ECHANTILLON DE PEINTURE MURALE

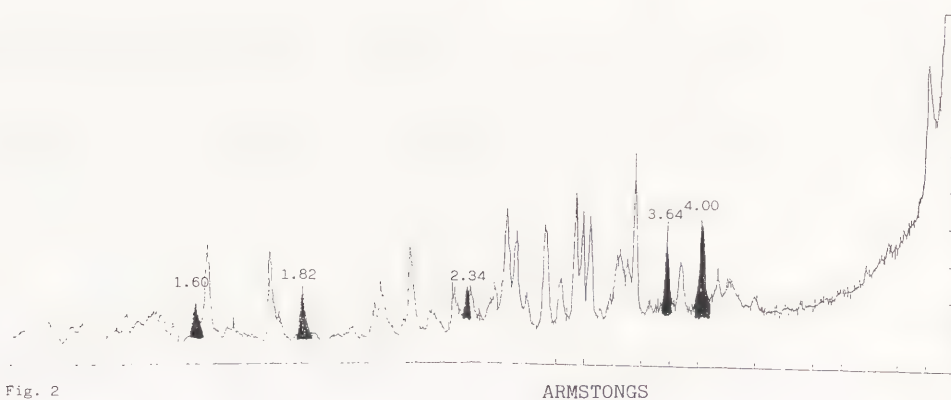
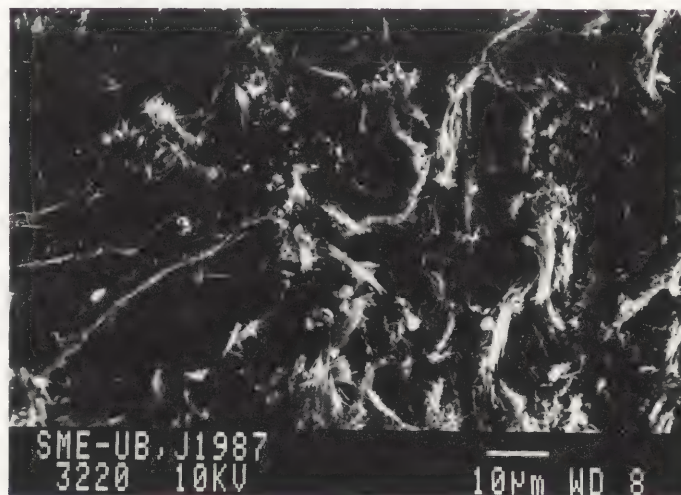
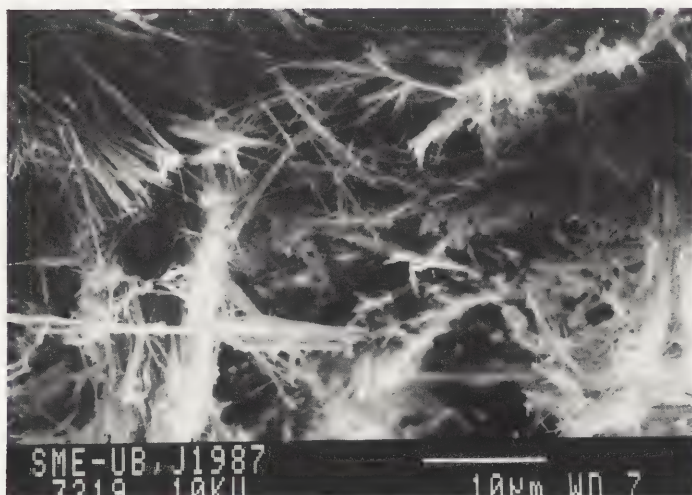


Fig. 2

DIFRACTOGRAMME DE RAYONS X D'UN ECHANTILLON DE MINERAL

Les sommets foncés correspondent à l'aerinite



ABSTRACT

The analytical study of samples taken from the Carracci frieze provided information on original materials and technique as well as on past retouchings and treatments which were responsible for obscuring the brightness of the original colours. The frieze is a true fresco painting without any addition in secco. The technique of Italian mural painting of the 16th century in comparison with that of previous periods is discussed, also taking into consideration technical investigations of other works and information given by antique treatises. The methods of the restorers of the past are also discussed.

KEYWORDS

Carracci, painting technique, mural painting, fresco, old restoration.

THE "STORIES OF ROMULUS AND REMUS": A FRESCO FRIEZE BY THE CARRACCI

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1. Introduction

The painted frieze is a form of decoration that ornaments the halls of many Bolognese buildings. These friezes, illustrating a story from history or mythology, occur all around the upper part of the internal walls. The narrative cycle is structured in various scenes that illustrate successive episodes of the story. Ornamental frames enclose the scenes separated by "putti", telamons, and/or architectural motifs.

This form of indoor decoration, previously developed in Rome and in northern Italy, was introduced into Bologna by Nicolò dell'Abate and Pellegrino Tibaldi, in the mid 1500's. Its success was rapid and fast growing, such that this form of decoration became a characteristic of private buildings in Bologna built or redecorated by both middle-class and noble Bolognese families (1).

Friezes in two Bolognese buildings, Palazzo Fava and Palazzo Magnani, were executed by the Carracci.

In 1584, at the beginning of their activity, the two brothers, Annibale and Agostino, and their cousin Ludovico painted the frieze in Palazzo Fava depicting the "Stories of Jason"; and shortly after, also painted the frieze in the adjoining room with the "Stories of Aeneas" (2).

Around 1590, the Carracci painted the frieze with the "Stories of Romulus and Remus" in the main hall of the "palazzo" of Lorenzo Magnani. The Magnani family, of modest origins, had achieved considerable wealth through various activities, especially in the banking field. Lorenzo Magnani also was able to combine political prominence with his wealth, obtaining, after much uncertainty and controversy, senatorial investiture directly from Pope Sixtus V. In order to celebrate the position achieved, Lorenzo commissioned the construction of a new splendid residence according to a design of Domenico Tibaldi, and called upon the Carracci to decorate the main hall with the frieze illustrating the story of the foundation of Rome.

The frieze of Palazzo Magnani represents the most complete work of the three famous painters and rapidly became a reference point for the Italian art world: testimony to the changes, "reform", they brought to the art of their time (3, 4).

2. State of Conservation Before Recent Restoration

The most serious damage suffered by the Carracci frieze was that caused by natural phenomena and by inadequate past restorations attempting to repair the damage.

Phenomena of subsidence had caused sinking of the walls, and cracking and breaking off of the plaster. Repeated attempts were made to repair the resulting damage with replastering and repainting. Before recent restoration cracks could be seen in some areas along with powdering and peeling of the plaster. In addition, extensive areas of the frieze appeared disfigured by darkened retouchings and by a surface film obscuring the original colours.

The Carracci frieze of Palazzo Magnani was recently restored by Ottorino Nonfarmale (5). On this occasion an analytical study of samples taken before restoration was carried out. The results are here reported.

This study allowed the materials used to be identified and provided information regarding the painting technique as well as the retouchings and surface additions that can be attributed to past restorations.

3. Sampling and Methods of Study

The samples examined come from two scenes: "The Shelter for Refugees on the Campidoglio" attributed to Agostino (Fig. 1) and "Romulus Tracing the Border of Rome with a Plow" attributed to Anni-



Fig. 1. Agostino Carracci, "The Shelter for Refugees on the Campidoglio", after cleaning.



Fig. 2. Annibale Carracci, "Romulus Tracing the Border of Rome with a Plow", after cleaning.

bale (Fig. 2). In addition, other samples from the accompanying decorations relative to these two scenes were taken from: the simulated monochrome trabecation at the base; the monochrome gargoyles that ornament the upper and lower frames of the scenes; the "Telamons" imitating stone sculptures, with adjacent fleshy "putti", intercalated between the scenes; the nude figures coloured to imitate bronze that protrude from the upper angles of the scenes themselves.

The stratigraphic structure of the samples was studied by observation of their cross-sections in incident and fluorescent light. Pigments and media were identified by microchemical tests, staining tests and by determination of pigment elemental composition carried out on the sample cross-sections using an X-ray energy dispersive spectrograph (EDS) connected to a scanning electron microscope.

4. Results

4.1. The Painting Technique

In almost all the samples examined, the original paint appears to have been applied in a single layer, with the exception of the samples taken from the frame where the paint frequently consists of two layers.

The medium is always and only calcium carbonate. The pigments identified are "bianco sangiovese" (lime white); ochre pigments in the usual range of yellow, red and brown shades; green earth; and smalt (blue glass coloured by cobalt oxide).

The fresco technique was used in both the main body and decorative parts of the scenes. This was suggested by the "in situ" observation of the evident characteristics of the "giornate" (the plaster applied day by day). The analytical results confirm this observation, and also show that a true fresco technique was used, without any addition in secco (tempera finishing when the wall had dried). In fact, calcium carbonate is the only medium in the original paint. This is a result that is necessary but not sufficient to distinguish whether or not the fresco technique was used, because analytically, the result would be the same in the case of a lime painting technique where the pigments mixed with lime are applied to dry plaster.

Even so, there are other indications that support the use of the fresco technique, and not only those arising from the "in situ" observation of the "giornate" profiles. Another indicative factor, for example, is the fact that in most of the sections examined there is no net division between the plaster and the paint. On the contrary, it is seen that the pigments more or less penetrate into the plaster, sometimes quite deeply, a phenomenon that occurs when dilute pigments have been applied on still very moist plaster (6).

Analogously, when there are two layers of paint, the absence of a clear separation between the layers, found for most of the sections examined, suggests that the second layer was applied when the first layer was still moist so that, although slight, some mixing occurred.

The nature of the pigments found and identified also is in agreement with the diagnosis of the fresco technique. All the pigments found can be used for fresco painting without danger of their alteration.

The stratigraphy indicates rapidity of execution, such as that required for the fresco technique; indeed the execution must have been particularly rapid because indications of any modification of that already painted by application of additional paint layers are rare.

Indeed, almost all the samples from the two central scenes and from the telamons and the adjacent "putti", show a single paint layer that presumably was applied in modulated hues to predetermined areas and then smoothing the junctions. So, for example, in a blue sky area a single layer containing smalt and a small amount of red ochre occurs (ochre addition was perhaps for obtaining a warmer hue). The clouds were not painted over the blue ground, but directly onto the plaster, in areas destined for them, by application of a very thin layer of sangiovese white.

The samples from different flesh areas (as well as the simulated stone of the telamons) also showed a single layer consisting of a similar mixture of pigments but with slightly

different hues, due to variable proportion of yellow and brown ochre mixed with sangiovanni white. A single flesh sample showed two layers, probably representing the junction between two areas of different hue.

It appears that the Carracci used the practice described by Cennino Cennini based on preparing three different shades of a given colour, light, dark and mid-tone and carefully applying them in the planned areas: "neither adding or subtracting from the area of one colour to another, except where they join" (7).

The modeling of the simulated bronze nudes that protrude from the scenes of Agostino and Annibale also was probably obtained by directly applying three different shades of green in adjacent areas. In fact the bronze paint consists of a single greenish layer containing green earth, black and a little yellow and brown ochre, with the only variation being in the amount of black pigment which is greater for those samples coming from shadow areas and less in those samples from light areas.

The careful division into areas of different hue does not seem, however, to have been the practice followed for painting the simulated monochrome trabecation at the base and the gargoyle decorations above and below the scenes. Indeed, for example, the samples from light areas in the trabecation show a single layer consisting of sangiovanni white mixed with a little black and yellow ochre (of quite similar composition in the two parts attributed to Agostino or to Annibale), while in the shadow areas, this layer is covered by a second one, also in fresco, containing a higher proportion of black and yellow pigments.

The attribution of the various parts of the frieze to Agostino, Annibale or Ludovico is a problem that has led to considerable discussion among art historians (3). There is no documentary confirmation in this regard, and Malvasia cites that which is supposed to be the reply of the artists when questioned about their individual contributions: "ell'è dei Carracci: l'abbiam fatta tutti noi" (it is the work of the Carracci: it was done by all of us)(8).

The results of the analytical study do not lead to any clarification of the problem of the attribution. No differences were found between the two scenes examined, one which the critics unanimously recognize as the work of Agostino and the other as that of Annibale. The materials used are similar, as are the pigment mixtures, the stratigraphic structure, and the painting technique. These similarities are again found in the decorative parts that frame the two scenes, areas where the work of assistants would have been more likely. At least in the parts of the frieze studied, it is not possible to distinguish the various "hands" that produced the work. All worked with a similar technique, probably agreed upon, thus supporting the phrase cited by Malvasia.

4.2. State of the surface

Evidence of later retouching was found in some of the samples examined. The retouchings generally appear much darker than the original paint underneath; the medium is for the most part tempera: it includes a protein substance not perfectly identified.

The presence of a grey-brown surface film containing protein was found in almost all of the samples. The protein substance is probably from glue applied in the past in an attempt to fix or give new life to the colour.

Animal glue with molasses added was the recipe advised in the last century by Secco Suardo to consolidate cracked plaster (9). And, certainly, in the past, glue was used to treat entire frescoes - for example those by Michelangelo in the Sistine Chapel (10) - presumably intended as a varnish destined to give new life to the colours and recover flattened relief.

The glue applied to the Carracci frieze, just as that used in the Sistine Chapel, altered with time, producing a grey-brown patina that obscured the images.

Confirmation of the existence of later retouchings and coating (hypothesized after the "in situ" observations) and the attainment of a more precise understanding of their nature was useful information to the restorer in a general sense, because it can be extended to other areas which were not sampled but which the "in situ" examination and cleaning tests indicate as being in

analogous conditions to those of the quite limited areas for which analytical results were obtained.

5. Discussion

The Carracci have been faithful to the traditional fresco technique codified by Cennino Cennini more than Cennino himself. Indeed Cennino in spite of his clear preference for fresco painting, pointed out that "all work painted in fresco must be finished and retouched in secco with tempera" (11).

As can be also seen from an examination of various works, the mural painting technique used in the 1300's and 1400's is in reality a mixed technique. Only some parts (e.g., the flesh areas) are painted entirely in fresco; other parts, more or less extended in area are painted in secco (in egg tempera or glue) on a fresco underpaint (12).

In this period, the blue areas - the sky, the Virgin's cloak - are always painted in tempera on a red or black fresco underpaint. This was necessary because the blue pigments available at time were only the very expensive ultramarine and azurite which alters rapidly in the alkaline environment of fresh plaster. The partial execution in tempera, however, was not only a technical requirement. Very often the finishing in tempera was very widespread and not only confined to the blue area; it could even be a tempera reworking that covered the fresco underpaint almost completely (13).

In the late 1400's and then in the 1500's, the fresco painting (more or less completed) in tempera was partly abandoned, and painting completely in secco with organic media of various types, often oil, was frequently preferred. But, at the same time, the most significant examples of true fresco are from this period. In the Sistine Chapel, Michelangelo essentially used only this technique, and with extraordinary ability, obtaining effects of transparency and chromatic richness never before reached in mural paintings of previous periods, effects that were concealed by later additions and which the recent cleaning has brought to light (14, 15).

By the end of the 1400's, a new, inexpensive, blue pigment suitable for fresco became available: smalt (Michelangelo also used this pigment). But this technical advantage does not seem to be the only explanation for the adoption of the true fresco technique. During the course of the 1500's, painters often yielded to the temptation of the easier, more practical secco technique but the superiority of the fresco technique was recognized. Testimony to this is given by Vasari who describes in detail how to paint in oil on dry wall (and he himself used this technique in the Palazzo Vecchio in Florence). But, at the same time, warns that "mural painting must be executed in fresco and never retouched in secco, because, in addition to being ignoble, this makes the lifetime of the painting shorter". Evidently, the Carracci shared the opinion of Vasari.

Various considerations can be made in regard to the state of conservation of the frieze.

First of all, once more it is worthwhile to emphasize the durability of true fresco painting. The original colours of the Carracci, just as those of Michelangelo in the Sistine Chapel, reappeared perfectly preserved after all the various additions of past restorations were eliminated. Unfortunately, this is not the case for many mural paintings of previous period where the parts painted in secco often have been lost, leaving black skies, only traces of decorative motifs, and figures that are a pale image of the original.

A second consideration regards the questionable role of many past restorations from both the technical and aesthetic points of view.

The method used to consolidate powdered plaster or to fill cracks does not seem to have been very effective, perhaps because of the materials used, and especially because of the way in which they were applied. Probably, it was not known or not taken into consideration that long-lasting effects can be achieved only by in-depth penetration of the consolidant (true for plaster just as it is for stone).

Deleterious consequences from an aesthetic point of view have resulted from the practice common in the past, for both wall paintings and easel paintings, of overlaying additional materials

rather than eliminating those which already had been applied to the original in previous restorations. The glue layers on the frescoes, just as the new varnishes (often purposely coloured) applied to panel and canvas paintings, may have, at first, given the impression of imparting new life to the colours, but these layers were destined only to conceal the original work.

The splendid and surprising results of the cleaning conducted with modern criteria are testimony of the extent to which the methods used by restorers of the past had disfigured the original works and obscured the brightness of their colours.

References and Notes

1. A.W.A. Baschloo, Il fregio dipinto a Bologna da Nicolò dell'Abate ai Carracci (Bologna: Nuova Alfa Editoriale, 1984).
2. Bologna 1584. Gli esordi dei Carracci e gli affreschi di Palazzo Fava (Bologna: Nuova Alfa Editoriale, 1984).
3. A. Emiliani, Le Storie di Romolo e Remo di Ludovico, Agostino e Annibale Carracci in Palazzo Magnani a Bologna (Bologna: Nuova Alfa Editoriale, 1989).
4. S.J. Freedberg, Circa 1600. Una rivoluzione stilistica nella pittura italiana (Bologna: Nuova Alfa Editoriale, 1984), translated from Circa 600. A Revolution of Style in Italian Painting, "Preston H. Thomas Memorial Lecture Series", Cornell University, Ithaca, N.Y. 1980.
5. O. Nonfarmale, "Intervento di restauro al fregio dei Carracci in Palazzo Magnani", in Emiliani, op. cit. n. 3, 195-196.
6. The penetration of the pigments into the plaster may be an erroneous diagnostic criteria because the penetration depends on many factors (the moisture content and the compactness of the plaster, the size of the pigment particles, the extent to which the paint has been diluted). It is possible that a fresco may present a net division between the plaster and the paint layer consisting of pigments bound with calcium carbonate. But when penetration of the pigments into the plaster occurs, and to so great an extent as in the present case, it is an indication that the fresco technique has been used (see Mora and Philippot, op. cit., n. 11, 28).
7. C. Cennini, Il libro dell'arte, cap. LXVII and LXX (Venezia: Neri Pozza, 1971), 79, 84.
8. C.C. Malvasia, La Felsina pittrice (1678) (Bologna: Tipografia Guidi all'Ancora, 1841), vol. I, 287.
9. G. Secco-Suardo, Il restauro dei dipinti (Milano: Hoepli, 1927), 549.
10. F. Mancinelli, "Il restauro degli affreschi di Michelangelo nella Cappella Sistina", in Problemi del restauro in Italia (Udine: Campanotto, 1988), 297-299.
11. C. Cennini, op. cit. n. 7, cap. LXXVII, 90-91.
12. P. Mora, L. Mora and P. Philippot, La conservation des peintures murales (Bologna: Editrice Compositori, 1977), 151-161.
13. For some examples of this mixed technique see:
L. Tintori, "Segnalazioni sul costante progresso tecnico nelle pitture murali di Simone Martini (1315-30?)", in Tecnica e stile: esempi di pittura murale del Rinascimento italiano, E. Borsook and F. Superbi Gioffredi eds. (Parma: Silvana, 1986), 11-16.;
D. Dini and G. Bonsanti, "Fra Angelico e gli affreschi nel Convento di San Marco (ca. 1441-50)", ibid., 17-24;
A. Del Serra, "Sodoma a Monteoliveto Maggiore e discussioni su tecniche miste, pigmenti e cartoni (ca. 1505-08)", ibid., 59-60.
Mural paintings of the 14th and 15th centuries that were found to have been produced by extensive secco painting on a fresco underpaint also are not lacking in Bologna: the Stories of the Magdalene by Vitale da Bologna in the Church of S. Maria dei Servi (see R. Rossi-Manaresi, Restauri a Bologna e Ferrara, Bologna: Nuova Alfa, 1986, 70-71) and the Adoration of the Child by Paolo Uccello in the Church of S. Martino (see R. Rossi-Manaresi, Rapporti della Soprintendenza Beni Artistici e Storici, n. 28 (Bologna: Alfa Editrice, 1981) 177-181).
14. N. Gabrielli, "Aspetti scientifici nel restauro degli affreschi di Michelangelo nella Cappella Sistina", Bollettino Monumenti Musei e Gallerie Pontificie, VII (1987): 151-162.
15. G. Colalucci, "Le lunette di Michelangelo nella Cappella Sistina (1508-12)", in Tecnica e Stile, op. cit., n. 13, 76-81.
16. G. Vasari, Le Vite, Introduzione, Della Pittura (Firenze: Sansoni, 1966), 128-130, 135-136.

ABSTRACT

The analysis of organic dopes in grounds and paints used in wall painting of a Middle Asia monument - Sultan Sanjar's Tomb - has been carried out. This monument is a unique piece of Oriental culture of the 11-12th centuries.

It is known that ancient craftsmen in Middle Asia introduced organic dopes into grounds and paints in order to improve their technical properties.

We have identified materials of grounds and paints of this monument and determined that they had been used as an organic dope.

A quantitative analysis of the organic dope in samples of wall painting has been carried out for the first time. We managed to extract and detect about 0.9% of dry protein.

KEYWORDS

Analysis of organic materials, wall painting, ground, minerals, organic binder, quantitative analysis.

IDENTIFICATION AND QUANTITATIVE ANALYSIS OF ORGANIC MATERIALS IN GROUND COATS OF WALL PAINTINGS IN SULTAN SANJAR'S TOMB

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Introduction

Sultan Sanjar's Tomb in Turkmenia is one of the most interesting 11-12th centuries monuments with wall painting on a gypsum base. Wall painting, as was shown by analysis, was placed on a rather thick ground coat - .3 to .5 cm. The ground coat was prepared on a gypsum binding and filled with clay, quartz, calcite, and sometimes, coal particles. The ground consists of several coats, the upper one under the painting, was smoothed particularly thoroughly and polished till it was almost shining. The analysis showed a noticeable amount of organic admixture. We suggested that this admixture might have been added as a retarder of gypsum setting, which enabled ancient masters to obtain an ideally smoothed surface under painting. A negligible thickness of painting colour coat, constituting .05 to .10 cm, and a small size of pigment particles indicated fine grinding of minerals for paints and their thin dilution.

The colour range of the painting is quite diverse: on sees red, blue, yellow, green, lilac and violet colours, and a multitude of their shades. Another investigation carried out at our institute /1/ was devoted to an analysis of mineral ingredients of paints used for Sultan Sanjar's Tomb wall paintings. We will just note here that minerals containing iron oxides and clay constitute the base of red and yellow pigments, lapis lazuli, that of blue pigment, malachite, that of green pigment, gypsum, that of white pigment, coal, that of black pigment. Bleaching and binding components in paint coats are also clay mortar along with an organic binding material.

It is known that Central Asian masters added various organic substances to clay mortar improving its technological properties. There is information available that such materials as plant juices, animal milk, sour milk and other substances were used for this purpose /2, 3/.

All the preliminary investigations such as microchemical tests, infra-red spectroscopical analysis, dyeing samples with active dyes, showed that we were dealing with protein-like additions.

A quantitative determination of the organic additions in the ground coats was done by the Lowry method /4/ and by an ordinary weighing analysis. The Lowry method was chosen by us owing to its high sensitivity: applying this method one can find protein in highly diluted solutions where the quantity of protein is expressed in dozens of microgrammes. The Lowry method is based on a change in the colour intensity of a solution in which a reaction to protein (Folin's reaction) goes on with tyrosine and cystine radicals of the protein molecule. Folin's reaction consists in the phosphoric-tungstic and phosphoric-molybdic acids mixture reduction (Folin's reagent) which results in a blue-coloured complex compound. The above reduction reaction is promoted by complex copper compounds created when protein reacts to an alkali solution of blue vitriol.

The solution optical density is measured by a spectrophotometer with 750 nm in 1 mm - thick vessels. The protein content in a tested sample is determined by a calibrating curve.

Samples of wall painting from different parts of the monument southern wall were selected for tests: sample 1 - the ground coat under a violet paint layer, and sample 2 - the ground coat under a red paint layer. Before being analysed samples were subjected to a tris - glycine poise, pH = 8.9, and dialysis against water. The analysis results showed that the protein quantity in samples constituted .28 percent on average. In spite of the fact that different weighted amounts of sample 1 were taken, the protein quantity results in samples are quite comparable with one another, as well as with the data on sample 2.

It was interesting to compare the data on sample protein content obtained by Lowry method with the weight analysis data. Samples of dry protein hydrolisate obtained for aminoacid analysis (Table 2) were used for weight analysis. According to these data the amount of aminoacids in sample 1 turned out to be

.27 mg/ml, and the protein quantity in the same sample, determined by Lowry method, constituted .15 and .15 mg/ml. The aminoacids mass values and the original protein mass, expressed in percentage to the weighted amount taken, are in approximately the same correlation: for sample 1 - .29 and .30 p.c. - by Lowry method, and .60 p.c. in weight analysis; for sample 2 - .26 p.c. --by Lowry method, and .89 p.c. in weighting analysis. The difference in the results is accounted for both by the share of water added in hydrolysis per each protein link and by a certain amount of unremoved inorganic admixtures. Despite this difference both methods are quite suitable for the quantitative estimate of protein bindings in painting samples.

The identification of the protein component in the samples tested was done by means of aminoacid analysis. The work consisted of several stages: extraction of a protein binding by the poise, purification from salts by dialysis against water, hydrolysis of protein in 6M HCl solution at 105°C for 48 hours, and hydrolysate analysis with Hitachi automatic device with subsequent processing of the data obtained.

Aminoacid analysis results are given in Table 3. The higher content of glutamic acid (12.5 p.c.), asparagine acid (11.6 p.c.) and lysine (8.0 p.c.) proves its similarity with aminoacid analysis of milk protein α -lactoglobuline (5.6). The higher lysine content indicates the absence of vegetable proteins, and the presence of sulphur-containing aminoacids indicates the absence of casein. It can be suggested that milk components, possibly milk wheys, were added to the painting and ground coat material of the monument. A fairly large content of such aminoacids as threonine (5.6 p.c.) and serine (6.1 p.c.) may show the addition of other proteins to the painting material too.

Table 1

Quantitative Determination of Protein by Lowry Method in a Wall Painting Sample of Sultan Sanjar's Tomb

Sample	Ground coat sample weighted amounts	Protein by Lowry in mg/ml	Protein quantity in p.c. to the original weight
Sample 1	308.0	.15	.29
	113.2	.20	.30
Sample 2	315.2	.15	.26

Table 2

Determination of Aminoacids Summary Mass by Weighing Method in Wall Painting Samples of Sultan Sanjar's Tomb

Sample	Ground coat weighted amount in g.	Aminoacids summary mass (dry protein hydrolysate)	Protein quantity in p.c. to the original weight
Sample 1	1.0951	6.6	.60
Sample 2	1.2538	11.2	.89

Table 3

Aminoacid Composition of the Binding in Painting Samples from Sultan Sanjar's Tomb

Name of aminoacids	Content in p.c.	
	Ground coat with paint layer	
	Sample 1	Sample 2
Tryptophan	-	-
Lysine	7.8	8.0
Histidine	3.3	3.9
Arginine	1.3	2.4
Cystine acid	-	-
Asparagine acid	11.6	11.5
Threonine	5.9	5.6
Serine	6.1	5.8
Glutamic acid	12.5	12.0
Proline	3.9	3.4
Glycine	8.6	9.6
Alanine	8.7	7.9
Cystine	3.3	2.2
Valine	6.2	5.6
Methyonine	7.8	4.8
Isoleucine	3.9	2.5
Leucine	3.3	2.5
Tyrosine	2.0	3.8

Bibliography

1. V.N.Yarosh and M.I.Filimonova. Investigation of Wall Painting Materials from Sultan Sanjar's Tomb. Moscow, 1984, 6. 1-6, Culture and Art in the USSR, series: 'Museum Activity and Protection of Monuments. Restoration and Conservation of Museum Valuables', Lenin State Library. Express Information, Issue 7.
2. N.M.Baginsky. Investigation and Mastering of Old Central Asian Architects' Materials and Methods. USSR Academy of Science Proceedings, 1941, vol. 30, № 3, pp. 278-281.
3. A.G.Logvinenko and M.A.Savinkina. Physico-Chemical Foundations of Production and Hardening of Binding Materials Made of Porous Gypsum Rocks'. Novosibirsk, Science, 1974, pp.41-46.
4. Yu.B.Filipovich and others. Practical Work in General Biochemistry. Prosveshchenie, 1982, pp. 67-69.
5. V.L.Kretovich. Plant Biochemistry. Moscow, Vysshaya Shkola, 1980, pp. 26-47.
6. E.Marshall. Biophysical Chemistry. Moscow, Mir, 1981, pp. 211-212.



Working Group 16

Resins: Characterization and Evaluation

Résines: caractérisation et évaluation



ABSTRACT

An evaluation of Parylene has been undertaken. This article is a progress report. Parylene has been found to be an effective consolidant for a number of materials, especially those which are too delicate to be treated by conventional procedures. Treatment is described for fossils, natural history specimens, textiles, paper, books and archaeological and ethnographic materials. Parylene has also proved useful in the treatment of burnt paper.

KEYWORDS

Parylene, polymer, consolidation, fossil, textile, archaeological conservation, ethnographic conservation.

PARYLENE AT THE CANADIAN CONSERVATION INSTITUTE-AN INITIAL SURVEY OF SOME APPLICATIONS

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1. Introduction

1:1 Why Interest in Parylene developed.

Interest developed when the Canadian Conservation Institute was requested to aid the National Museum of Natural Sciences (in Ottawa, Canada) in the conservation of a collection of unusual fossils from Axel Heiberg Island in the Arctic. Here, in poorly consolidated Tertiary deposits, lie the remains of ancient (ca. 40 million years old) subtropical forests. There are stumps, fallen trees and leaf-mat, containing many species of leaves, ferns, cones and seeds. Despite their age, the fossils are non-mineralized and sometimes non-compressed, but tend to become extremely delicate on drying. Some have the consistency of cigarette ash.

Normal consolidation procedures were unsuitable because of the extreme delicacy and complexity of the specimens. It was thus necessary to consider unconventional approaches. There were reports by Humphrey of the use of Parylene which suggested the method might have promise (1,2).

1:2 The Parylene Method.

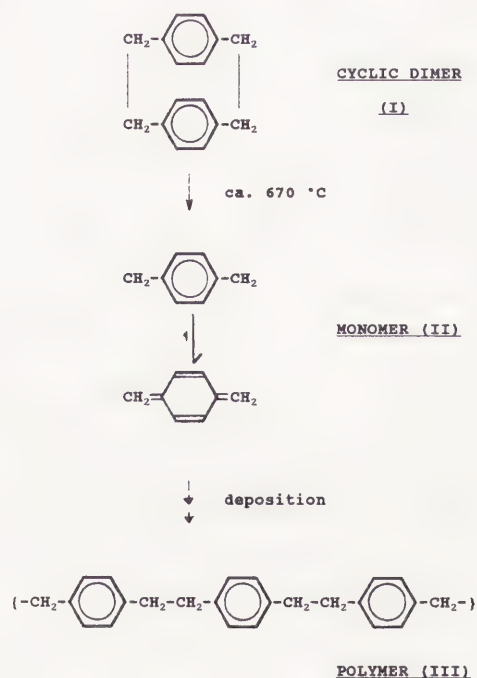
The method creates thin, even and transparent films of poly-para-xylylene (Parylene) on surfaces (3). Films conform to irregularities and thus a coated surface retains morphology which means that appearance changes very little after coating. This is seen in fig.1 which shows scanning electron micrographs of a butterfly wing before and after application of 0.25 μ Parylene N. Films have useful consolidant properties in the range 0.25 to 20 μ .

1:3 Deposition.

Deposition of the Parylene takes place under vacuum. It consists of:

- a) the vaporization of the cyclic dimer (I)
- b) the pyrolysis of the dimer at 670 \pm 20 $^{\circ}$ C, to form the monomer (II),
- c) diffusion, deposition and polymerization of to form a coherent film.

Gaseous monomer diffuses into the fine structure and thus porous structures and inner surfaces are coated. Two types of Parylene are commonly used: "N" is unsubstituted, whereas "C" has one chloride on each aromatic ring. Parylene C is used in most applications because it has better mechanical properties, but if better diffusion is required, as with a book for instance, Parylene N is used. Film thickness, which is adjusted by varying the weight of Parylene dimer placed in the apparatus, can normally be controlled to \pm 1 μ .



1:4 The Initial Trial.

Ten fossil cones were taken to the Nova Tran (4) laboratory in Wisconsin for trial treatment. Placed under vacuum in the coating

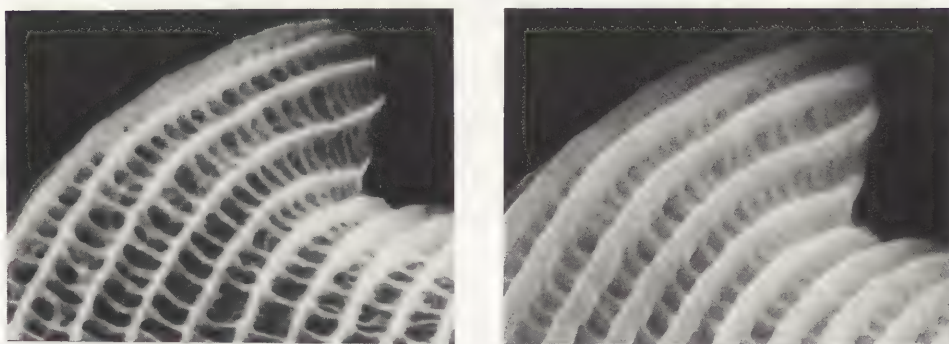


Figure 1. Scanning electron micrograph of butterfly wing before and after Parylene coating. (figures are 12μ across).

apparatus, they were watched closely as moisture evaporated. This is a precarious phase because warping and fragmentation is possible. They survived intact but with some opening of the scales. Fortunately, this enhanced rather than diminished the appearance. No other changes were observed during the deposition.

The cones, which were effectively strengthened by Parylene, appeared unaltered by the coating. The presence of Parylene was not obvious to the touch. The Parylene was hardly evident when the cones were viewed with a stereo microscope. This "invisibility" of the Parylene probably results from the way it conforms to the surface. In thin section at higher magnification, however, the Parylene is clearly visible as a very even birefringent layer.

2. Applications:

The success of the method led to a wider study in which various museums and galleries in the Ottawa area evaluated the process with a wide variety of fragile objects, specimens and materials. In assessing the effectiveness and suitability of the procedure we relied completely on the judgement of the conservator, preparator or curator who brought in the specimens. Some quantitative measurements were also taken and these include: colour change by tristimulus colour measurement (Minolta Chromameter), surface gloss by gloss meter (flat surfaces only), response to RH change and weighing. In addition to the evaluation, thermal and light aging studies have been initiated. This work is the result of collaboration between many people, and this is a progress report rather than a finished work.

2:1 Textile conservation.

Satisfactory strengthening of delicate disintegrating silk textiles was achieved with Parylene C. With coatings below 2μ the textiles remained flexible, but above this they were stiff enough to affect the drape. Generally, Parylene was not evident, but for certain shiny silks, interference fringes were noticeable with 1, 2 and 3μ coatings, but not with 5μ . It was observed that in addition to film thickness, the weave structure of the fabric affected flexibility. Open weave fabrics remained flexible with thicker coatings of Parylene whereas tightly woven fabrics became unacceptably stiff with thin coatings.

2:2 Book, paper and library conservation.

Books. The recommendation given by Nova Tran for books is that they receive 8μ Parylene N. For coating, books are mounted in a clamp which holds the end boards vertically with the book fully open. Under vacuum the pages fan out allowing access of monomer vapour. Some distortion may occur as moisture evaporates under vacuum. After coating, books return to shape after a day or two. We found that dry books regained moisture at exactly the same rate whether coated or not. Books are very slightly thicker after coating, but there is generally little alteration in appearance.

Tests have been made on alternative ways of mounting books. Those with very weak (e.g. paper) or weakly attached end-boards have been placed on their spines with the pages fanning out in a vertical arc. The results have been satisfactory.

We found that the Parylene thickness varies considerably throughout books. Films are thicker at the edges of pages and thinner towards the hinge. On pages with very smooth surfaces, such as colour plates, the uneven films sometimes cause interference fringes. These are noticeable as a series of faintly coloured rings, focused approximately at page centre. On end

boards, which usually have non-porous surfaces, adhesion is often poor. Scratching with a fingernail lifts the Parylene which shows as a white line. This effect is largely preventable with the adhesion promoter (Union Carbide A-174, an acrylic monomer containing a silane). When added to the deposition chamber it spreads evenly over all surfaces, and polymerizes. Books so treated pass the scratch test.

Use of a phenolic anti-oxidant, which has been shown to extend the service life of Parylene, gave an alarming result with certain books. Bright yellow colouration developed in regions of heavy degradation. It appears as if the anti-oxidant interacts with a degradation product of the paper. Fortunately Parylene is so stable, as discussed below, that the anti-oxidant is unnecessary.

Paper. Materials studied include: Ashless paper (Whatman filter paper), newsprint (groundwood), offset book (bleached), alkaline register paper, latex saturated surface coated and embrittled book paper.

In addition to standard procedures mentioned above, testing includes measurement of basis weight change, calliper, "zero-span" tensile strength, cross section tearing strength and bursting strength. Half of the acidic samples have been deacidified prior to coating.

Paper is strengthened noticeably by Parylene. With a sample of newsprint, zero span tensile strength increased 28% in the machine and 46% in the cross direction, burst strength increased by 170% and tear strength by 42%. In manual fold tests, however, it has been noticed sometimes deteriorated paper can break more easily after coating.

The aging study of treated paper has not yet begun, but will include humid oven aging and light exposure studies.

Red rotted leather end boards. We have been consulted about a large collection (ca. 10,000) of 19th century ledgers with leather bindings which are badly red-rotted. As an alternative to re-binding, with consequent loss of the original binding, we have investigated the possibility of Parylene consolidation.

A binding with text block removed, received 2 μ of Parylene C. This stopped the crumbling of the surface completely. A ledger with text block in place was then tested. The text block, in good condition, was wrapped in plastic film (Saran Wrap) to prevent it being coated. Consolidation by 2 μ of Parylene was again satisfactory, and the text block remained Parylene free. Experiments continue, but it is clear that the method is able to consolidate the disintegrating bindings.

2:3 Natural History Specimens.

2:3:1 Arctic Plant Fossils.

Cones: In the initial trial, mentioned above, cones representing a number of conditions from very delicate spruce to rather flattened metasequoia were tested. Coated with 12.8 μ of Parylene C, the results were considered successful as explained. In subsequent work, it was found that for some cones, particularly the large spruce, the attachment of scales was poor.

In another experiment, 3.6 μ Parylene N was used initially to diffuse into and strengthen the cone before a final coating with Parylene C to 13.7 μ . Attachment of scales was much improved.

Colour measurement has not been possible with cones, because of their fragility (ie before coating), surface irregularity and size. Observations of colour with the leaf mat sections, which have similar surfaces (given below), show that colour is little altered by coating.

Leaf Mat Sections: Leaf mats vary considerably from a highly compressed semi-coalified state in which leaves are not easily distinguished, to non-compressed non-coalified with each leaf and cone preserved as a distinct entity. As with the cones, the leaf mats become excessively fragile on drying.

Several procedures were tested, and each type of mat required a different approach. Two examples are as follows:

Sample 11, though non-coalified and composed of distinctly separable metasequoia leaves, was quite well consolidated. After

treatment with 8.7 μ of Parylene N for good penetration, no change in size took place and consolidation was good.

The colour measurements shown in Table 1, (by Minolta Chromameter using the D6500 luminance standard) indicate a slightly less reflective, i.e. darker, surface with a very slight trend towards blue. This confirms visual assessment of little change.

Sample 4 was coalified with wood inclusions and had poorly resolved leaves. A portion fragmented on drying under vacuum and the wood inclusions warped badly. It was thus decided to treat another piece with polyethylene glycol to prevent the cracking and distortion caused by moisture loss in the coating process.

Another portion, soaked in a 30% v/v solution of polyethylene glycol 200 for 3.5 months, was chilled to -40°C and freeze-dried at -20°C . No warping of wood inclusions took place and it was then coated with 26 μ Parylene N. Fragmentation of the section was eliminated and no delamination or separation of the Parylene film has since occurred.

Table 1.
C.I.E colour coordinates for leaf mat sections.*

X	x	Y
<i>before Parylene</i>		
11.58	.3365	.3402
<i>after Parylene</i>		
7.37	.3301	.3321
* Average of seven determinations.		

2:3:2 Fragile Mineralized plant and animal fossils

A problem with several kinds of mineralised fossils is their tendency to crack in response to relative humidity change. It was hoped that Parylene might help to eliminate this and this effect has been investigated as part of the evaluation.

Fossil bone. Appearance was unaltered by coating and Parylene inhibited dimensional response to relative humidity (RH) fluctuation. (This is not considered a suitable procedure for fossil bone, however, since most are too big and there are alternative procedures.)

Mammoth horn. Parylene did not stop the RH related dimensional change.

Flaking cuticle on Shale. Flaking cuticular material on an unstable inorganic (shale) matrix was coated with Parylene C and N. The change in appearance was negligible, and the flaking was inhibited, but the Parylene did not prevent the shale from delaminating as RH changed.

It was concluded that, though a number of problems remain, Parylene has application in the stabilization of mineralised fossils in shales.

2:3:3 Crustacea and other marine organisms.

Crustacea and marine organisms tend to become very brittle as they dry out and age: sponges have fine spicules which readily break off, spine on sea urchins and setae on crabs do the same, corals tend to lose sections and break. Parylene C at about 7 μ has been found to consolidate these effectively with minimal alteration of appearance. The most convincing demonstration of the effectiveness of Parylene was with a crinoid, which was so fragile that sections broke off with vibration in car during transport. It could not be handled without breakage. After coating with 16.1 μ Parylene C, it was completely strengthened and could be handled easily.

2:3:4 Insects

A number of insects were coated with very good effect, they were much stronger and tended not to lose components. The Parylene is easily observable by SEM as shown in fig. 1, and the conformal nature is very evident. The consolidation is very effective, but coatings have to be thin to avoid changing the appearance. Antennae are in the region of 1-5 μ in thickness, thus coatings must be below 2 μ . Iridescence on butterfly wings is lost.

2:3:5 Display specimen preparation.

The use of Parylene in preparing Natural History specimens for use in displays and dioramas etc. has been investigated. Generally, the results were satisfactory, it was found that Parylene added

strength to delicate specimens. There were some problems: the Parylene tended to show as a whitish layer with thicker coatings, and finer structures such as fins, fibres and fluff on seeds were visibly thickened. For such characteristics as strength, consolidation, durability and natural appearance Parylene is successful at certain thicknesses. This is determined by the nature of each specimen and the desired effect. In some cases appearance might be of secondary importance to strength and durability and sometimes vice-versa. Parylene could be used in the preparation of a wide range of plant and animal specimens to allow display or withstand frequent handling.

Some specific observations are noteworthy:

Glycerin treated leaves. Parylene coating delaminated on glycerin-treated leaves and on plants containing natural oils such as the leaves of eastern white cedar.

Insects. There was a loss of iridescence on butterfly wings, but not on a "greenskin beetle".

Feathers. Clumping (or matting) of feathers on stuffed birds was noticeable at thicknesses of 15μ Parylene C but not at 6.4μ .

Spider's webs. Spider's webs were successfully coated, but were still delicate.

Living plants. Fresh plant material tended to shrivel up.

2:4 Archaeological and Ethnographic Objects.

Few applications have been identified for ethnographic and archaeological conservation. For many materials the main problem is caused by moisture loss. If this could be minimised the warping and damage would be lessened. Experiments will continue with higher deposition pressures to minimise moisture loss, and thinner coatings.

The following examples show some of the problems which arose:

Disintegrating shredded Cedar Bark. This is a common problem in North West ethnographic objects. 2μ of Parylene C gave good consolidation of individual fibres whereas 4μ caused the bark strands to mat together.

Fur. The desiccation caused by the vacuum produced irreversible contraction and hence distortion of the skin. At present Parylene can not be used to address such problems as hair slippage etc.

Dry powdery pigments. Experiments were conducted to consolidate dry powdery pigments on various substrates, including leather, parchment, bark and cedar. Parylene stabilized the pigments and with 4 and 8μ films it was not noticeable. On evacuation and desiccation, the substrates tended to warp badly.

Wet and fragile archaeological textiles. For the Parylene experiments, very degraded wool textiles from burials in Red Bay, Labrador were used. These shed fibres continuously whether mounted or not. They were very filthy and were washed until mushy. Coating with 4.4μ Parylene C or 5.5μ Parylene N gave very acceptable consolidation without alteration of appearance. There was a suggestion of surface bloom and a slightly crunchy feel. Further shedding was prevented. It has been noted that samples like this could be dealt with by adding Parylene in stages, thin-layer by thin-layer. Thinner deposition should prevent the bloom and crunchiness. Thin coatings may allow further cleaning of very finely divided dirt under the microscope.

2:5 Burnt Paper.

Parylene has certain forensic applications: In particular it can strengthen burnt paper effectively. Several kinds of paper, marked with different inks, were charred in a furnace till blackened as if burnt. After treatment with 4 and 8μ of Parylene C, the paper appeared unaltered, yet could be handled roughly without damage. Analytical techniques for deciphering lettering etc. including examination by infra-red and ultra-violet light were unaffected by the presence of Parylene.

A batch of water-soaked and burnt books from a recent air crash was freeze-dried and then subjected to treatment with 6 - 12μ of Parylene N. The pages, although strengthened did not stick together and separation was facilitated by the Parylene.

3 The stability and reversibility of Parylene.

3:1 Reversibility:

Ideally, materials for conservation should be easily and completely removable, so that if treatment fails re-treatment is possible. Failure to meet this criterion is not a valid reason for rejecting Parylene because there are other considerations. Parylene strengthens delicate materials effectively and has the potential to preserve materials for which there is no other method. It may also conserve materials in a way which is superior to normal procedures. Furthermore, lack of removability may not prevent further treatment such as re-consolidation or adhesion to a support.

3:2 Stability of Parylene:

Recently, it has been shown that Parylene is very stable (5). These data indicate that Parylene N should survive in darkness at 25 °C for ca. 2000 years, and Parylene C for 130,000 years before 50% of the strength is lost. Yellowing does not occur until after the film has failed mechanically. Stability to light has been studied recently (6) and it has been found to be sensitive to ultra-violet light but less so to visible. It is noteworthy that Parylene films, as normally employed, are thin compared to other consolidants or varnish films and yellowing may be imperceptible.

4. Conclusions.

Parylene has been shown to have a number of uses in conservation. There are a number of problems which it alone has the capacity to solve. The thinness and invisibility of the coating, the control with which it can be applied and its great stability compensate for many of the difficulties posed by the irreversibility of the process. We hope that this initial evaluation has shown certain areas where it can be useful and these will be investigated in more detail once the evaluation is complete.

Acknowledgements.

To the Union Carbide Corporation for technical help and the loan of a Parylene apparatus, and to colleagues who collaborated in the project. Thanks to: Paul Bégin (The National Archives of Canada), Monique Papineau, (Archives nationales du Québec), Gerry Fitzgerald, Len Marhue and Ron Seguin (National Museum of Natural Sciences), Helen Coxon (Royal Ontario Museum), Cliff McCawley, Scott Williams, Tom Strang, Season Tse, Malcolm Bilz, Ela Keyserlingk, Judy Logan and David Tremain (Canadian Conservation Institute), Dan Purdy (Royal Canadian Mounted Police). John Garstang (Canadian Aviation Safety Board). Special thanks to Robert Barclay and Margaret Morris (Canadian Conservation Institute) who operated the Parylene coater for extended periods, and to Bruce Humphrey and other staff at Nova Tran for their help.

Notes

1. B.J. Humphrey, "The Application of Parylene Conformal Coating Technology to Archival and Artifact Conservation", Studies in Conservation, 29 (1984) 117-123.
2. B.J. Humphrey, "Vapor Phase Consolidation of Books with the Parylene Polymers", J. American Institute of Conservation, 25 (1986) 15-29.
3. S.M. Lee, "Xylylene Polymers", Kirk Othmer Encyclopedia of Polymer Technology, (John Wiley, New York) 3rd Edition, 24, 744-771.
4. The Nova Tran Corporation is a part of the Union Carbide Corporation, which specialises in Parylene applications.
5. D.W. Grattan and M. Bilz, "The Thermal Aging of Parylene, and the effect of Anti-Oxidant", to appear in Studies in Conservation.
6. E.F. Hansen and W.S. Ginell, "The Conservation of Silk with Parylene C", in Historic Textile and Paper Materials II, Conservation and Characterization, ACS Symposium Series 410, ch 8, pp.108-13 (1988).

ABSTRACT

Commercially available aliphatic polyfunctional isocyanates (such as Mobay Corporation's Desmodur N-3390 (R), a prepolymer of hexane-1,6-diisocyanate) and other chemically related systems show promise in the consolidation of a wide range of cultural materials. Based upon preliminary experimental results and the chemical literature, particularly suitable materials may include adobe, stone, paint on ethnographic objects, leather and wool. The polymer, a polyurea, may be formed *in situ* by reaction with atmospheric and adsorbed water. It is colorless with resistance to yellowing and degradation. There is ample opportunity for modifying the physical properties of the polymer by incorporating urethane linkages through the use of polyhydroxy compounds as co-reactants. Unlike many other reactive monomers (typically volatile silanes) which are difficult to use on a large scale, the prepolymer of hexane-1,6-diisocyanate, an isocyanurate with three pendant isocyanate groups, is not volatile and with normal care is safe to use. The low cost, and consistency of quality of the product, offer particular advantages for further developmental work in this area of conservation. The Getty Conservation Institute is actively pursuing some of these research directions.

KEYWORDS

Isocyanate, polyurethane, polyurea, moisture-curable resin, aging, structure/property relationship, consolidation, adobe, paint, collagen, keratin.

CONSOLIDATION WITH MOISTURE-CURABLE ISOCYANATES:
POLYUREAS AND POLYURETHANES

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Introduction

Polymers play an important role in conservation as adhesives, binders, coatings, consolidants and for other uses. Yet little effort is being made to evaluate new polymers for the field, especially commercially available ones. This reluctance probably stems from caution regarding reversibility, uncertainty about aging characteristics, lack of knowledge about possible interactions of a polymer new to conservation with the substrate, and unavailability of test facilities for evaluation of processing materials. The Resins Working Group of ICOM has encouraged exploration in this area, and the Scientific Program of the GCI has for some time been active in doing just this. For example, Parylene-C and a new range of fluorinated polyimides have been evaluated, and work was about to start on an interesting new thermoplastic adhesive, PEOX, (1) when the manufacturer withdrew it from production.

We believe that there is ample scope for the cautious introduction of polymer types new to conservation, and that commercial products with possible conservation applications should be constantly under evaluation. We review here preliminary work on aliphatic isocyanate-based polymers which cure *in situ* by reaction with moisture, and suggest possible applications in conservation, based both upon our observations and the chemical and conservation literature. These polymers have been under active investigation for several years at the GCI as potential adobe consolidants, and are also being tested for terracotta, stone, and particularly salt-deteriorated substrates, in which promising results are being achieved in consolidation followed by desalting.

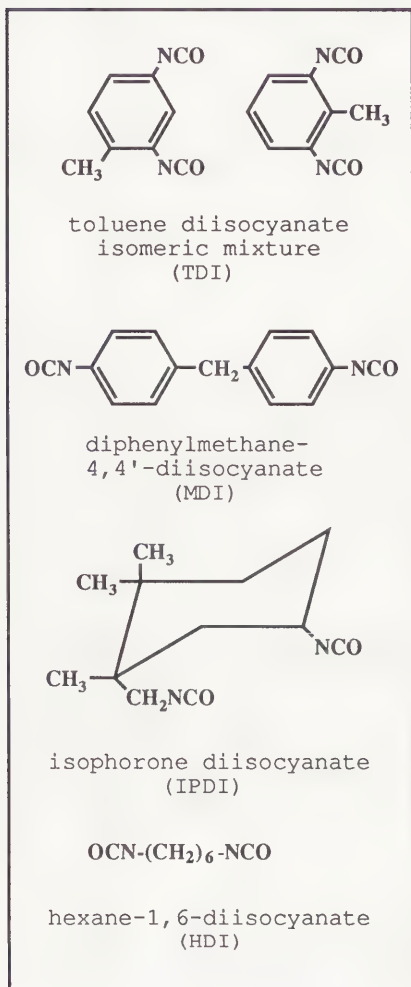
The isocyanate-based polymers are closely allied chemically to polyurethanes which have become enormously important industrially over the last 40 years or so. Today, they have a range of applications including flexible and rigid foams, elastomers, adhesives, binders, lacquers, cellular coatings, vulcanization of natural rubber and other uses. (2) (3) The applications result from the multitude of end products which can be obtained by varying the two chemical components of a polyurethane: a hydroxy functional compound and a diisocyanate. (4)

By far the largest use of polyurethanes in conservation has been as a foam support, with applications ranging widely from protection of objects in transit to a backing for the transfer of wall paintings or mosaics. Polyurethanes have also been considered as an adhesive or consolidant for stone, concrete, brick, wood, leather and plastics; and as a protective coating for stone, wood or stained glass. A moisture-curable polyurethane has seen use in Japan for the consolidation of deteriorated wood objects or buildings. (5) An innovative use of a moisture-curable polyurethane is in Scotchcast(R) tape, a knitted fiberglass fabric impregnated with a polyurethane resin. (6) This tape, developed for use in the medical profession, is also capable of setting underwater and is used to lift and support waterlogged and other fragile materials from archaeological sites.

In situ polymerization

Polymeric consolidants, such as Acryloid B72, that are applied in solution have several disadvantages associated with high molecular weight, viscosity, reverse migration of the polymer to the surface on evaporation of the solvent, and the non-interaction of the polymer with the substrate. The last consideration may be regarded as an advantage by conservators when reversibility is important. In such instances the polymer is a "spectator" molecule in the substrate - it merely acts to tie together the substrate mechanically without chemically linking to it. But, for effective consolidation a chemically bonded polymer is inherently better than an inert one, despite the lack of reversibility.

Figure 1. Isocyanate monomers



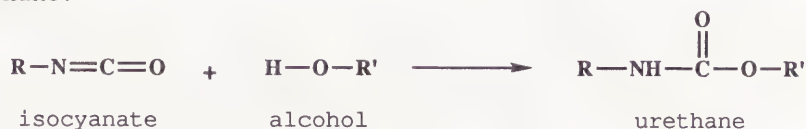
On the other hand, reactive systems that polymerize *in situ* offer advantages even when higher molecular weight prepolymers are used. In this category viscosity may be a problem, as with some epoxy resins, but the theoretical ideal is achieved in a consolidant polymerized from a one-part system; a monomer that can be polymerized *in situ* to yield a polymer intimately associated chemically, or mechanically, or both, with the substrate. Several such systems have been used for some time now in conservation: the alkoxy- and alkylalkoxysilanes (for example, tetraethoxysilane and methyltriethoxysilane), and methylmethacrylate. The latter is difficult to polymerize *in situ* because of the inhibition of the free radical polymerization by oxygen; stress-related cracking of the substrate may occur when polymerization is done below the glass transition temperature of the polymer. The silanes are almost unique because of hydrolysis with atmospheric moisture - the reaction yields a volatile alcohol and ultimately (though the reaction may take years to complete) a silicon-oxygen polymer. The economic and practical disadvantages of these volatile monomers are the cost and high loss to the atmosphere through evaporation when work is done outdoors.

We are investigating the chemically simple isocyanate system - a single reactive component, that appears to have several advantages for consolidation of a range of substrates. The most significant advantage of an isocyanate is the ability to polymerize by reaction with atmospheric and adsorbed moisture. Prepolymers of aliphatic isocyanates are commercially available, which have well established characteristics and quality control of production. The cost of the prepolymer is moderate to low by comparison with silanes. Our work has been directed to conservation of large structures, specifically adobe and outdoor sites, in which substantial quantities of consolidant would be needed. The unique properties of the aliphatic isocyanate system have prompted us to investigate a wider variety of substrates, not only because results relevant to the conservation of these substrates have, to some extent, been determined in the industrial arena, but also in order to draw these to the attention of the conservation community so that further evaluation can be undertaken in other laboratories.

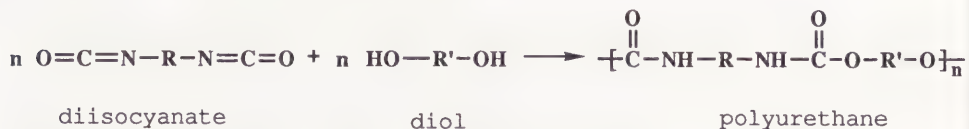
Chemistry

The isocyanate group is extremely reactive with compounds containing active hydrogen atoms (by definition those compounds that yield methane upon reaction with methylmagnesium iodide). Thus, free molecules containing isocyanate are not found in nature.

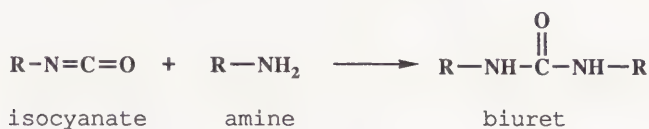
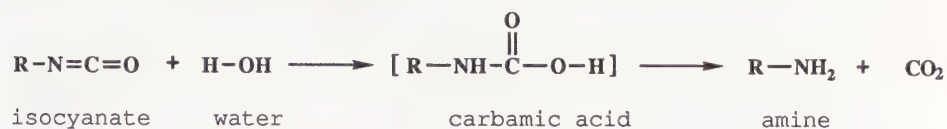
The reaction of an isocyanate with an alcohol produces a urethane:



By the same reaction, diisocyanates, and in general polyfunctional isocyanates, react with dihydroxy and polyhydroxy compounds to form polyurethanes:



Besides the urethane reaction above, isocyanates have other reactions with active hydrogen compounds. Some of the most important are:



In addition to establishing the stability of a material with desirable properties for consolidation, application procedures or methods must exist for adding the resin in the desired concentration and distribution without adversely affecting the object, either immediately or in the future. Suitable solvents must be determined because the viscosity, wetting ability, and volatility of solutions may affect the penetration, spreading and adhesion of the consolidant. Isocyanate prepolymers require solvents which are polar and do not contain active hydrogens. The range of solvents is limited, but includes methylethylketone, butylacetate and chlorinated hydrocarbons. However, solvent mixtures have also been used successfully. Inert diluents (such as xylene) may be added up to 50% of the solution composition.

Applications

We have previously commented on the use of isocyanates for the consolidation of adobe.(11) General requirements for the consolidation of outdoor earthen structures are environmental stability, high strength, depth of penetration and unchanged appearance. In certain circumstances, permeability to water-vapor or moisture is necessary to reduce stress at the interface of consolidated and unconsolidated regions. A major problem with any consolidant for an adobe structure is swelling of the unconsolidated, interior adobe which can cause the consolidated outer layer to crack and delaminate from the existing structure. The polyurea obtained from HDI is undergoing field testing on adobe structures.(12)(13) Another problem with the consolidation of adobe is a darkening of the surface. Laboratory tests have determined that the change in appearance differs with solvent mixtures, which may indicate that the problem lies in the method of application and not with a specific property of polyurea. A further difficulty is the rigidity and strength of the consolidated layer. Flexibility may be improved by incorporation of polyoxyethylene glycols(PEG), which results in the formation of some urethane linkages. Flexibility of the resin increases with an increase in the molecular weight of the PEG, and also depends upon the amount added. Molecular weight grades of 200 to 10,000 are readily available. We are pursuing this line of research as some success has already been achieved in the modification of polyurethane properties for medical purposes, where both flexible and strong materials are desired.(14)

Tests are underway to evaluate the desalting of salt-laden terracotta consolidated with Desmodur N 3390 (R). Repeated attempts to wash the salt away will reveal if the treated clay is still water permeable, and also if it has been successfully consolidated. Preliminary tests on terracotta, and also brick and adobe, have been successful and a quantitative extraction of salt has occurred.

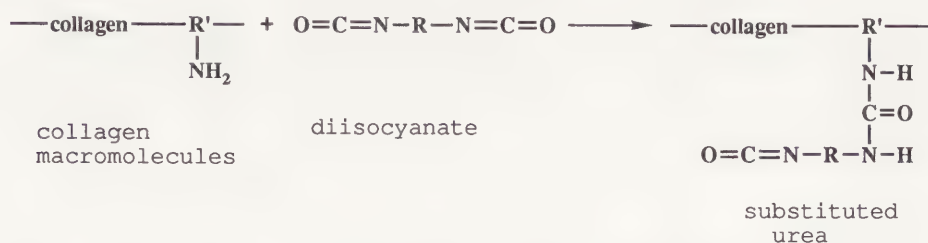
The consolidation of painted ethnographic objects is difficult because darkening and discoloration often results from the addition of a resin to a porous matte paint.(15) High strength polymers, that might achieve consolidation by use of a minimum amount of added resin, may reduce the darkening and changes in gloss. In such a system, reversibility is of little concern and thermosetting resins are under consideration.

In initial attempts at consolidation of kaolin and red ochre on paper substrates with dilute solutions (<3%) of Desmodur N 3390(R) in methylethylketone, both consolidation of the clay and ochre, and also adhesion of paint to the paper substrate, was achieved without noticeably affecting the matte surfaces. This resin is undergoing further evaluation by comparing the extent of appearance change and consolidation achieved with equivalent amounts of thermoplastic resins (acrylics, poly(vinyl butyral)) commonly used for consolidation, and other thermosetting resins (epoxies).

Isocyanates may be especially useful in the treatment of degraded collagen and keratin because consolidation may be achieved through intermolecular crosslinking resulting from covalent bonding of the isocyanate group with an active hydrogen in the collagen or keratin macromolecule.

Traubel has commented on the use of diisocyanate monomers, and investigated the use of hydrosol urethane oligomers (based upon HDI) for industrial applications in the treatment of leather.(16) They were explored for use as a tanning agent alone, as a pre-tanning agent, for re-tanning, and as an aid to dyeing. The diisocyanate monomers themselves are too toxic for many conservation applications, but similar reactivity and end products should result from using isocyanate prepolymers, which are less hazardous due to their lower volatility.

The isocyanate reacts with basic groups in the collagen macromolecule, presumably to form a substituted urea consisting of the diisocyanate used and the collagen backbone:



This substituted urea still contains an isocyanate group which may react with water, leading to polymerization, or with another collagen molecule, resulting in cross linking.(17)

Polyurethanes are used as building blocks for artificial leather, and are also used for leather coatings due in part to high water-vapor permeability, flexibility and tensile strength. Thus many possibilities exist for their use in the conservation of leather. Moisture-curing polyurethanes have been proposed as a consolidant for the conservation of leather bindings of books.(18) There is a need to impregnate weakened leather with a resin which will provide support and reinforcement. Lankrothane 1304 (R), a commercially available moisture-curable polyurethane, shows some promise for consolidation.

In addition to the consolidation of bookbindings with moisture-curable polyurethanes, furskins with a tendency to tear in certain areas were strengthened by treatment with isocyanates, or isocyanates mixed with plasticizers. The tear resistance was increased when the weaker areas were sprayed from the skinside with diisocyanates in chlorinated paraffins.(19)

Moisture-curable polyurethanes improve the crease retention and water repellency of wool. Guise compared the shrink resistance, physical properties and aging of wool treated with polyurethanes polymerized from aliphatic and aromatic isocyanates, and different molecular weight PEGs and diols.(20) Interestingly, in this system moisture-cured polyurethanes formulated from PEGs showed a reverse trend in the oxidative stability of polyurethanes, in that the wool treated with polyurethanes with aromatic substituents had better oxidative stability than the wool treated with polyurethanes with aliphatic substituents. Effective treatment was obtained at very low (approximately 1%) levels of applied polymer.

Moisture-curable polymers may be useful in treating deteriorated wool, because of the combined benefits of added strength from cross-linking, the possibility of designing a flexible consolidant, and the lack of shrinkage resulting from *in situ* polymerization.

Conclusion

Moisture-curable consolidants are being tested for uses in conservation that cannot be adequately served with the currently available and tested thermoplastic resins. The technology of polyurethane and polyurea chemistry has advanced to the point where these resins can be considered for particularly difficult problems associated with the consolidation of deteriorated or fragile materials. Significant considerations are:

1. the availability of environmentally stable aliphatic isocyanates;
2. opportunities to tailor the physical properties of polyurethanes by varying both the isocyanate and the polyol;
3. and the unique advantages that result from using a moisture-curable monomer that polymerizes *in situ*.

Results of research conducted at the Getty Conservation Institute on the consolidation of adobe prompted the evaluation of moisture-curable polyureas for the consolidation of a similar material, porous or powdering paint on ethnographic objects. The consolidation of leather, wool and other proteinaceous materials is considered because of the unique advantages offered from *in situ* polymerization and the greater degree of consolidation that is afforded from intermolecular crosslinking. Though these systems are widely diverse, they are similar in that no currently available materials or methods are entirely suitable for the problems encountered in their consolidation.

The commercially available product that we have most intensively tested for the consolidation of these materials, Desmodur N 3390 (R), is not the only aliphatic isocyanate commercially available. The low cost of this material makes it particularly desirable for large, earthen structures. However, other commercially available moisture-curable prepolymers may have other desirable properties. These might also be considered when the amount of consolidant used is relatively small, as in objects made of clays, leather or wool.

Materials

Desmodur N 3390(R), Mobay Chemical Corporation, Pittsburgh, Pennsylvania 15205, United States. (412)-923-2700.

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Notes

- 1 Suggested by Andrew Thorn, 2/43 Coppin Grove, Hawthorne, Melbourne, Australia 3122.
- 2 G. Wood, The ICI Polyurethanes Book (Chicago: ICI Polyurethanes and John Wiley and Sons, 1987), 1-6.
- 3 A. H. Hughes, "Polyurethane Resins in Moisture Curable Surface Coatings," Journal of Oil Colour Chemists Association 1 (1986): 10-14.
- 4 G. Oertel, Polyurethane Handbook (Munich: Hanser, 1985), 11.
- 5 S. Higuchi, "Consolidation and Restoration of Deteriorated Wooden Materials with Synthetic Resins," in Conservation of Wood (Tokyo: Organizing Committee of International Symposium on the Conservation and Restoration of Cultural Property, 1978) 23-32.
- 6 A. Calver, "Scotchcast Casting Tape," Conservation News, 31 (1986): 12.
- 7 G. Wood, The ICI polyurethanes Book, 50.
- 8 D. Lasovick, Urethane Coatings (Philadelphia: Federation of Societies for Coatings Technology, 1970), 18.
- 9 A. Moncrieff, "Abstract No. 13-314," Art and Archaeology Technical Abstracts 13, no. 1, (1976): 82.
- 10 Bayer, Desmodur N 3390, Order No. LS 4409e (Germany: Bayer, 1984), 1-3.
- 11 N. Agnew, Adobe Preservation (Los Angeles: Getty Conservation Institute, 1987), 55-59.
- 12 N. Agnew, F. Preusser and J. Druzik, "Strategies for Adobe Preservation, The Getty Conservation Institute," in 5th International Meeting of Experts on the Conservation of Earthen Architecture, ed. C. Rockwell (Rome: ICCROM, 1987) 3-12.
- 13 N. Agnew, J. Druzik, T. Caperton and M. Taylor, "Adobe: The Earliest Composite Material," in ICOM Committee for Conservation, Preprints of the 8th Triennial Meeting, Sydney ed. K. Grimstad (Los Angeles: Getty Conservation Institute, 1987) 439-446.
- 14 E. W. C. Wong, "Development of a Biomedical Polyurethane: Orthopedic Implant Applications," in Urethane Chemistry and Applications ed. K. N. Edwards (Washington, D.C.: American Chemical Society, 1980) 439-446.
- 15 E. Hansen, E. Sadoff and R. Lowinger, "A Review of Problems Encountered in the Consolidation of Painted Ethnographic Objects and Potential Remedies," in ICOM Committee for Conservation, Preprints of the 9th Triennial Meeting, Dresden ed. K. Grimstad, in press.
- 16 H. Traubel, "Tanning with Isocyanates," Associaci on Quimica Espagnola de la Industrio del Cuero, 29 no. 6 (1978): 183-195.
- 17 Oertel, Polyurethane Handbook, 530-546.
- 18 British Library Manufacturers' Research Association, The Conservation of Bookbinding Leather (Hatfield: Stellar Press, 1984), 35-42.
- 19 W. Werner, Stabilizing Fur Skins, Patent DD 144793, (German Democratic Republic, 1980).
- 20 G. B. Guise and M. A. Rushforth, "Structural Studies of Shrink Resist Polymers for Wool: Polyisocyanates with Different Backbones," Journal of the Society of Dyers and Chemists, (1976): 17-21.

ABSTRACT

Synthetic, low molecular weight resins that have properties comparable to dammar, a natural low molecular weight resin, are described. To date, ketone resins are the only materials from this broad class of resins that are commonly used by conservators as substitutes for natural resins. The values of individual materials within this class of resins are illustrated so that conservation scientists can possibly modify adhesives, consolidants and finishes more to a conservators liking.

KEY WORDS

Tackifying resin, Gloss modifier, Aldehyde resin, Hydrocarbon resin, Ketone resin, Rosin esters, Terpene resin.

THE INDUSTRIAL USE AND DEVELOPMENT OF LOW MOLECULAR WEIGHT RESINS: AN EXAMINATION OF NEW PRODUCTS OF INTEREST TO THE CONSERVATION FIELD.

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Background

Towards the middle of the twentieth century, dammar, mastic and other natural resins were known as "nonconverting low molecular weight resins" to industrial and academic circles [1]. The terminology describes a class of highly amorphous materials which lack either the appropriate unsaturation or the functional groups that promote polymerization to higher molecular weights. At that time, industries used large quantities of these natural resins in adhesive recipes, textile sizings, and coating and ink formulations. One source, published in 1942, states that the U.S. was importing between 15 and 20 million pounds of dammar resin annually [2]. With the widespread production of synthetic low molecular weight resins shortly afterwards, industrial demand for this type of resin soon declined.

Today, the synthetic materials which replaced natural resins are classified as tackifying resins and as gloss modifiers [3,4]. The molecular weight, refractive index and softening point of these materials are comparable to their parent, natural materials. Because they are available with a discrete range of properties, synthetic low molecular weight resins offer more subtle variations than natural resins. This selection allows for improved servicing of a broader range of applications.

Tackifiers modify the optimal temperature, pressure and time (dwell) required to activate pressure sensitive and heat seal thermoplastic adhesives [5]. Tackifying resins impart a component of stiffness to an otherwise soft, flexible material, thus enabling an adhesive not only to flow but also to maintain its integrity after initial formation of the bond. A simple example is the use of tackifiers in rubber/resin pressure sensitive adhesives: a mixture of these materials creates an adhesive that has both fluid like and solid like components- two vital characteristics of pressure sensitive and heat seal adhesives. Pressure sensitive adhesives demonstrate these properties at ambient temperature while heat seal adhesives have to be brought to their activation temperature.

More complicated systems are based on di- and tri-block copolymer type adhesives where one of the phases is a rubber, or other soft, low glass transition material. Their activation parameters are modified by choosing a low molecular weight material that is selectively compatible with one of the copolymer microphases [6]. A narrow molecular weight distribution and a site specific polarity allow tackifying resins to work effectively. By matching the polarity of the domain, the resin automatically coalesces into this phase while a narrow molecular weight distribution facilitates this action [7]. Natural resins because of their greater polydispersity and chemical heterogeneity are miscible to varying degrees with both domains and therefore do not impart any beneficial properties to this type of adhesive.

Gloss modifiers enable pigmented coatings to achieve a higher level of gloss, improved body and flow, and shorter drying rates. They can be added to alkyd, nitrocellulose, urethane or vinyl paints. The light fastness of the modifying resin chosen depends on the color of the paint; if it is a pigment that is light in color, a more stable resin is chosen, but if the pigment is dark, a cheaper, less stable modifying resin could be used. In general, polar low molecular weight resins tend to be used more often as gloss modifiers because of their compatibilities with the above mentioned paints. Recently, aliphatic gloss modifiers have been undergoing rapid developments as a result of environmental constraints on volatile emissions [8].

It is apparent from the earlier literature that industrial applications have relied on natural resins in many formulations. Recipes which call for these resins were used in street marking paints, printing inks, the first pressure sensitive adhesives, as well as in many coating recipes in which their purpose was clearly for gloss modification [9]. With the advent of di- and tri-block copolymers, along with an enhanced understanding of polymer material science, a demand for new low molecular weight resins was created. This paper describes industrial applications of these new materials, and in addition explores some of the possible benefits these modifications may bring to conservation.

2 Synthetic Low Molecular Weight Resins

Some intrinsic qualities of resins can be determined by the starting materials used in the synthesis. For example, resins derived from unmodified terpenes and other hydrocarbons are nonpolar and therefore soluble in aliphatic solvents while insoluble in low alcohols (e.g. methanol and ethanol). On the other hand, resins derived from polar starting products will yield materials that are more likely to be soluble in polar solvents. The molecular weight distribution, glass transition temperature, and stability are properties that are further dependant on the mode of synthesis.

The point in common with all of these synthetic materials is that they are either cyclic, or highly branched species that when polymerized terminate to a low molecular weight; hence the final product is oligomeric. They should not be confused with oligomers such as novalacs and resols that are intermediates, known as interpolymers, to high molecular weight products [10]. The branched or bulky molecular structure not only accounts for a rather high refractive index, but also causes the materials to be amorphous. Since amorphous materials are not as efficiently arranged as crystalline materials, their reduced intermolecular interaction is a feature that in addition to their low molecular weight allows them to be soluble in higher concentrations.

Synthetic resins currently available range from easily oxidized polyterpene resins to other resins that are more expensive and considerably more stable to thermal and photochemical degradation. Technical information provided by the manufacturer typically contains resin-polymer compatibilities, solubility data, acid or bromine number and an indication of stability through either color change upon heat and sometimes light exposure. These materials have number average molecular weights from about 300 to 1000 with a fairly narrow molecular weight distribution and refractive indices of about 1.50 to 1.55.

2.1 Polar Resins

Aldehyde, ketone and ester modifications of gum and tall oil rosin are polar resins: due to the increased polarity these resins can have higher glass transition temperatures provided other properties remain unchanged. They are soluble in a broad variety of solvents ranging from acetone, ethanol and higher alcohols to hydrocarbon solvents of strong to moderate aromaticity. Recipes of high solids coatings incorporate substantial percentages of these resins into their formulas in order to reduce viscosity and improve flow while increasing resin content. These materials are also used to improve substrate wetting of ethylene-vinylacetate adhesives.

Laropal K-80, a ketone resin manufactured by BASF is synthesized from the condensation of cyclohexanone and formaldehyde. Synthetic resin AP is a ketone resin manufactured by Huls, made from the condensation of acetophenone and formaldehyde. Synthetic resin SK is a reduced form of synthetic resin AP. These resins are found in many formulations because of their reasonable stability and their broad compatibility with many high molecular weight polymers. Ketone resins are the only materials within the class of synthetic, low molecular weight resins that are commonly used by conservators as varnishes [16]. Laropal K-80 is also used as a modifier to the ethylene vinyl acetate heat seal adhesive, Beva 371, which was developed to be a lining adhesive for paintings [11]. It is worth noting that heat seal adhesives were introduced in 1965 by industry as an alternative to wax-resin adhesives [12].

Aldehyde resins available from BASF are condensation products of aliphatic aldehydes and urea, consequently these structures have amide groups as the source of their polarity. Laropal A81, A101, ALR8786 are aldehyde resins which offer improved U.V. stability while maintaining about the same solubility and compatibility characteristics as ketone resins. The purpose of these resins is therefore to act as a replacement for ketone resins where additional U.V. stability is required without sacrificing the broad compatibility characteristics required by some operations. Because of their similarity to ketone resins, aldehyde resins are under investigation as possible replacements of natural resins in picture varnishes [13].

Huls also manufactures a hydrogenated version of resin SK (Resin BL1280) that retains the aliphatic hydroxyl groups while the aromatic unsaturation is hydrogenated. This produces a material that is soluble in aliphatic solvents while having a higher T_g, due to hydrogen bonding. At a specific concentration, this resin undergoes a sudden, enormous jump in viscosity due to the occurrence of strong intermolecular hydrogen bonding. This quality is useful in printing and pen inks that must dry quickly: by including this resin in an ink formulation the ink sets up quickly with minimal solvent loss.

Rosin esters are typically too yellow to be used in light colored surface coatings and are therefore limited to primer coatings and other non-appearance related applications. Some rosin esters have been used as gum bases, and others where a high degree of tack over a broad temperature range is required. Hercules and Arizona Chemical market their rosin esters for applications where thermal stability is more important than the relative light-fastness of ketone resins.

2.2 Non Polar Resins

A thorough account of the development, synthesis and use of these resins is described by Koencke [14]. In his discussion he includes some of the attributes these materials have over natural resins.

Non polar resins lack carbonyl and hydroxy groups; this accounts for their insolubility in such polar solvents as acetone and ethanol. These resins are compatible with the aliphatic or aromatic hydrocarbon domain of ethylene-vinyl acetate (EVA), styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) copolymer adhesives. For example, aromatic hydrocarbon resins typically associate with the styrene domain while saturated hydrocarbon resins associate with the butylene or isoprene domain of SBS and SIS tri-block copolymers. Hydrocarbon resins are occasionally used as gloss modifiers to printing inks and other surface coatings, but adhesive applications account for the bulk of their use.

2.2.1 Unsaturated Hydrocarbon Tackifying resins

The least stable type of synthetic low molecular weight hydrocarbon materials are polyterpene resins. Zonarez (Arizona Chemical) products are manufactured from α & β pinene resins and possess good properties for common hot melt formulations. Polyterpene resins have been modified with both an aromatic and limonene copolymer portion. Examples of these resins are Nirez (Reichhold) and Zonatac (Arizona Chemical) respectively. The aromatic modified resins offer improved compatibility with styrene copolymers and the limonene modified materials are more thermally stable. All of the terpene resins are light or water white in color in their supplied form but have a tendency to degrade in the presence of U.V. light. Because of their eventual tendency to yellow, these materials are reserved for applications where appearance is not vital or use is short-lived.

The remaining hydrocarbon resins are based on C9 hydrocarbon fractions. The primary C9 starting material is α -methylstyrene, used to produce Resin 18 (Amoco) and Krystalex (Hercules). These resins have similar applications as cheaper terpene materials, but because of the methylation of the H, they are of superior stability.

2.2.2 Hydrogenated Hydrocarbon Tackifying resins

Hydrogenation for increased stabilization was recognized as early as 1940 when the hydrogenation of coumarone indene resins yielded materials that were "extremely resistant to ultra-violet light and atmospheric oxidation... which have to withstand the action of acids, alkalis, fruit juices and alcoholic beverages" [15]. The more recent development of hydrogenated hydrocarbon materials has been spurred on not only by a demand for materials that have improved U.V. and thermal stability, but also by requirements of rules such as the Los Angeles County Rule 66. This legislation is fostering the development of materials that are soluble in aliphatic solvents because these solvents are least likely to react with U.V. light to form smog.

The hydrogenated hydrocarbon materials currently available are converted from cracked C9 or C10 petroleum fractions and converted into oligomers. Arkon (Arakawa Chemical) and Regalrez (Hercules) products are based on isomers of C9 unsaturated carbons, while Escorez (Exxon) products are based on dicyclopentadiene, a C10 molecule. In each case, once the feed stock is polymerized it is then hydrogenated under high pressure and temperature to remove nearly all of the unsaturation. Hydrogenated hydrocarbon resins are under investigation as varnish materials because of their stability and their unique solubility properties [13].

3 Discussion: Some Possible Conservation Related Applications

There are circumstances where works of art requiring treatment have greatly benefitted from the introduction of synthetic materials. On the other hand, there have been occasions where the application of new materials and processes have interfered with the esthetic qualities of objects.

Sensitivity to these esthetic concerns and understanding conservation techniques and materials will help reduce the misapplication of new materials.

Dissatisfaction over the stability of natural resin varnishes has caused some conservators and artists to use more stable synthetic materials. Polyvinyl-acetate and poly alkyl-methacrylate varnishes have not been thoroughly embraced by conservators because of their less desirable optical and handling properties. After evaluating the differences between natural and synthetic resins, it has been determined that low molecular weight, high refractive index coatings are most capable of making matt substrates appear saturated and glossy [16]. The only synthetic resins commonly used by conservators that satisfy these criteria are ketone resins. Their use has recently been discouraged because of their tendency to oxidize and yellow [17]. It is possible that some of the products intended to replace ketone resins in industrial formulations may likewise be better ingredients for picture varnishes.

The new synthetic materials currently being tested as alternatives to natural resins may offer additional benefits, however, their success may be dependant on the development of new working methods. Ignoring the complexities of natural resins and simply substituting synthetic resins in their stead are likely to produce results that are unsatisfactory. Although synthetic resins have about the same molecular weight and refractive index of natural resins, impurities and other chemical/physical properties such as chain branching coefficient and molecular weight distribution may have a profound effect on their handling properties. With this in mind, successful application of these materials is likely to be contingent on new working methods.

Among the entire class of synthetic low molecular weight resins most have refractive indices below those of natural resins known to conservators, but some have values that are higher [13]. Therefore, it should be possible to visually evaluate the importance refractive index has on the optical appearance of varnished paintings if one could consistently control the varnish handling properties of a sampling of resins representing a range of these refractive indices. While it is generally stated that a high refractive index is important for the appropriate optical appearance of a varnish, exactly how high or near to natural resins has yet to be systematically evaluated.

The ketone resin component included in Beva has improved its substrate wetting, helps lower the activation temperature and reduces the risk of cold flow. These are substantial improvements over the wax resin adhesives used earlier. The yellowing of ketone resins may be of little significance where lining adhesives are concerned but may pose serious risk when applied to the backs of thin, translucent materials (e.g. paper). Replacement of ketone resin with an aldehyde resin should give a composition less prone to yellowing without altering the activation conditions too much. On the other hand, converting to adhesive recipes that rely on hydrocarbon resins will produce non yellowing adhesives that require different parameters for activation. Consequently, the properties of formulations that become indirectly modified have to be thoroughly evaluated before one can confidently use them.

3 Conclusion

From the literature that marks the transition from natural to synthetic resins, it seems as though industries have viewed most natural resins as imperfect materials, frequently trying to refine certain aspects through the development of synthetic resins [14]. To conservators the opposite seems to reflect the attitude of many; to them these new materials have lost some, though not all of the similar traits of natural resins. In spite of the shortcomings of synthetic low molecular weight resins, their diversification can still be of value to conservators and scientists that want to evaluate the various molecular attributes of natural resins; with the judicious selection of synthetic resins one can be aided enormously in confirming what are the truly important aspects of natural resins. Such progress may even lead to the development of synthetic resins that have properties that more closely meet a conservators criteria.

It is not a coincidence that low molecular weight materials continue to be used by such disparate groups as artists, conservators and a variety of industries; it is merely a recognition that only these materials are capable of imparting a certain behavior. It is this authors opinion that these materials have been under-utilized in conservation: for example, while there are a variety of high polymers used as adhesives and consolidants in conservation, very few are modified with low molecular weight resins. It is hopeful that in the future, conservation related recipes will profit using these materials the same way they have improved the specialization of many industrial formulations.

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Suppliers

Amoco Chemical Corporation, 200 Randolph Drive Chicago, Illinois 60601, USA.
Arakawa Chemical (USA) Inc., 625 N. Michigan AVE. Suite 1700 Chicago, Illinois 60611, U.S.A.
Arizona Chemical, 1001 East Business Highway 98, Panama City, Florida 32401.
BASF, Aktiengesellschaft, D-6700 Ludwigshafen, West Germany.
Exxon Chemical Company, P.O. Box 201, Florham Park, New Jersey 07932-0201.
Hercules Incorporated, Hercules Plaza, Wilmington, Delaware 19894.
H.l.s, Aktiengesellschaft, Postfach 1320, D-4370 Marl, West Germany.
Reichhold Chemicals Incorporated, 525 N. Broadway, White Plains, N.Y. 10603.

References

- 1 C.L. Mantel, "Natural Resins" in Film Forming Compositions, eds. R. Meyers and J.S. Long (New York: Dekker, 1967) part I 341-390.
- 2 C.L. Mantel, The Technology of Natural Resins, (New York: Wiley, 1942) 31.
- 3 J. Schladerman, "Tackifier Resins" in Handbook of Pressure Sensitive Adhesives, ed. D. Satas (New York: Van Nostrand Reinhold, 1982) 353-369.
- 4 E.W. Flick, Handbook of Paint Raw Materials, (New Jersey: Noyes, 1989)
- 5 C.A. Dalquist, Adhesion (London: Maclaren and Sons, 1969) 143-151.
- 6 J.B. Class and S.G. Chu, The Viscoelastic Properties of Rubber Resin Blends I. The Effect of Resin Structure, Journal of Applied Polymer Science, 30 (1985) 805-814.
- 7 J.B. Class and S.G. Chu, The Viscoelastic Properties of Rubber Resin Blends II. The effect of Resin Molecular Weight, Journal of Applied Polymer Science, 30 (1985) 815-824.
- 8 S. Paul, Surface Coatings (New York: John Wiley and Sons, 1985) 308-309.
- 9 C.L. Mantel, The Technology of Natural Resins (Brooklyn: American Gum Importers Association, 1939) 65.
- 10 J.A. Brydson, Plastics Materials (London: Butterworth, 1975) 514.
- 11 G. Berger, Heat Seal Lining of a Torn Painting with Beva 371, Studies in Conservation, 20 (1975), 126-151.
- 12 W.C. Wake, Adhesion and the Formulation of Adhesives (London: Applied Science Publishers, 1982) 275-280.
- 13 E.R. de la Rie and C.W. McGlinchey, New Synthetic Resins for Picture Varnishes, Submitted for publication to the IIC 13th International Congress, Brussels (1990).
- 14 D.F. Koenecke, "Hydrocarbon Resins" in Film Forming Compositions, eds. R. Meyers and J.S. Long (New York: Dekker, 1967) Volume 1, part I, 265-306.
- 15 H.R. Fleck, Plastics (Brooklyn: Chemical Publishing Company, 1945) 298-299.
- 16 E.R. de la Rie, The Influence of Varnishes on the Appearance of Paintings, Studies in Conservation, 32 (1987), 1-13.
- 17 E.R. de la Rie and A. Shedrinsky, The Chemistry of Ketone Resins and the Synthesis of a Derivative with Increased Stability and Flexibility, Studies in Conservation, 34 (1989) 9-19.

ABSTRACT

A group of Italian Renaissance bronzes at the Metropolitan Museum of Art, New York, were examined to determine the compositions of the surface patinas present. Micro-samples taken from the surfaces were subjected to Gas Chromatography/Mass Spectrometry (GC/MS), X-Ray Diffraction (XRD), and Energy Dispersive X-Ray Spectrometry (EDS). Separate samples of the underlying metal were subjected to EDS to obtain elemental compositions of the bronzes. Organic material was detected on all bronzes and identified by mass spectral evidence. In some cases plausible media for the application of patinas were suggested by the analyses. Difficulties in interpreting the analytical results are discussed. Elemental compositions of the bronzes showed promise for indicating geographical attribution.

KEYWORDS

Bronze, Drying oil, EDS, GC/MS, Natural resins, Patinas, Shellac.

SURFACE COMPOSITION OF SOME ITALIAN RENAISSANCE BRONZES

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Introduction

The small bronzes of the Italian Renaissance have a long tradition of art historical study and connoisseurship (1-8), including a fine appreciation of their surface patination. Despite this there has never been a systematic technical study of the patinas and methods of patination. Although many of the original surfaces of these bronzes have undoubtedly been altered through the ravages of hostile environmental conditions and overzealous aesthetic intervention it is felt that no complete description of these bronzes can exist without taking into account their surfaces: how they may have been prepared originally and their subsequent fate. Especially interesting are those bronzes which appear to have been patinated with tinted organic lacquers: golden yellow or ox-blood red and chestnut brown almost black. To investigate the composition of these putative lacquer patinas Gas Chromatography/Mass Spectrometry (GC/MS) was chosen as the major instrumentation as it requires only microscopic samples for the detection and identification of organic materials.

Samples were taken from a small group of Italian Renaissance bronzes in the collection of the Metropolitan Museum of Art, Department of European Sculpture and Decorative Art, which were judged from appearance to have been given organic lacquer-like patinations. The samples were of two kinds: one from the patina layer; one from the metallic surface on the underside of the object for determination of elemental metal composition.

The patina layer samples were subjected to GC/MS analyses after extraction and derivatization at the National Gallery Scientific Department (London), for the determination of organic components. Specimens of the patina layer were also obtained for X-Ray Diffraction (XRD) analyses and Energy Dispersive X-Ray Spectrometry (EDS) analyses to determine inorganic components (crystalline material by XRD; elemental composition by EDS).

Metal specimens from the underside of the sculpture, cut with a burin, were subjected to EDS analyses to determine the elemental composition of the bronzes.

Table 1 lists the bronzes studied (1-8), Metropolitan Museum of Art accession numbers, brief identification, and sample designations used at Metropolitan Museum of Art Objects Conservation Department (NY) and National Gallery Scientific Department (London).

Table 2 lists the kinds of analyses performed on the samples and the type of results reported.

Experimental

GC/MS. The results were obtained in two stages. 1) Samples were extracted with ether or benzene, methylated with diazomethane, and the methylated extract subjected to GC/MS. 2) The ether/benzene insoluble material was saponified with methanolic potassium hydroxide, acidified, esterified with diazomethane, and the resulting soluble portion analysed by GC/MS. Preliminary cleanup was carried out in some instances by chromatography on a short column (constructed from a capillary pipette) packed with deactivated silica gel. GC/MS procedures have been described previously (9, 10).

XRD. X-ray diffraction of most microsamples failed to reveal identifiable inorganic pigments. A sample from Met02,03, Antoninus Pius of Antico, showed copper oxides.

EDS ANALYSES. All samples were carbon coated and affixed to carbon stubs. EDS analyses were conducted in an Amray 1600T Scanning Electron Microscope (SEM) with attached Kevex 7000 microanalyser. The semi-quantitative analytical routine "ASAP" was used to obtain the weight percent of elements in each analysis. Operating conditions were 15-30 kV, 200 s collection time, 25 μm^2 or 10 μm^2 collection area; beam current was adjusted to give ca 25% "dead time." The general procedures have been described (11, 12).

Results

Table 3 summarizes results obtained from GC/MS analyses. All samples examined contained very little organic material and most of the compounds identified by GC/MS were at the threshold of detection. In all cases organic material was found. The variety of components found suggests that a large number of patination procedures were employed rather than a limited number. Most surfaces displayed at least some evidence that a drying oil (linseed or

walnut) was present. Also observed were Venice turpentine, pine resins, and bituminous material. Residues of later polishing probably accounts for the presence of beeswax, ceresine, and non-drying fats.

The footnotes of Table 3 supply the major mass spectrometric fragments on which the identifications of the organic materials are based. Those samples identified as containing conifer resins (MET01 and MET12) on the basis of methyldehydroabietate alone must be regarded with caution in view of the absence of its oxidation product, 7-oxodehydroabietate. In one case larixol (a component of Venice turpentine) was identified confidently by finding four characteristic mass fragments; in another case only three of the fragments were found.

GC/MS data obtained from the surface specimens present problems of interpretation. It appears that a negative result is less reliable in describing organic surface composition than a positive result. Some reasons that a negative result (absence of evidence) must be treated with less confidence than a positive result (even trace presence of mass-spectral fragments):

1. The surfaces are obviously nonuniform; a representative sample may not be obtainable.
2. Later polishings or restorations may have removed or altered the original patina.
3. Patination may be so highly crosslinked or admixed with inorganic material that the extraction process fails.
4. The patination may be so thinly applied that the small sample size fails to give sufficient extractable material.
5. The extraction process may fail for some of the mixtures actually applied as patinas.

Table 4 lists the EDS results obtained from 16 metal samples cut with a burin from the undersides of the bronzes. The bronzes contained copper (>80%; 2 samples <80%), tin (<10%; 1 sample >10%; 1 sample 0%), and lead (ca 1-40%). Three samples contained small amounts of zinc; three samples contained small amounts of antimony. Other trace metals (<1%) found were iron (13 times), silver (2 times), and nickel (1 time).

Four Veneto-Paduan bronzes have zinc and/or antimony (MMA Sample Nos. 3, 4, 14, 16); only one central Italian bronze has either (MMA Sample No. 11, zinc). The rest are all lead-tin bronze. Although the total number of samples examined is small, the division by school and geography is striking. It would be interesting to enlarge the data base with drilled samples and improved analytical procedure (e.g. atomic absorption).

Table 5 presents EDS results from samples of the patina layer. Normalization factors (ca 0.7 compared to ca 1.0 for the metal samples in Table 4) obtained from the software routine (ASAP) for collecting data strongly support the likelihood that the patina samples contained substantial amounts of organic material. All the samples gave high quantities of copper and small amounts of iron. Each sample also contained calcium, silicon, potassium, and sulfur. Aluminum and chlorine (except for one example each), magnesium, zinc, and phosphorus are frequently observed. Although lead occurred in every bronze sampled, only one showed it in the patina layer. The persistent presence of sulfur suggests the possible presence of sulfates and/or sulfides in the patina layer. Although every effort was made to sample the patina layer only, there is no way to know whether the sample is free of corrosion products or cleaning materials from treatments subsequent to workshop patination.

Discussion

The bronzes were chosen to meet two major criteria: that they have broadly accepted attribution to specific sculptors or well defined schools; that the bronzes would appear (visually) to have organic patinas of age appropriate to the period of manufacture. Even if all the examples did not have old or original patinas it was hoped that either some characteristic patination materials would emerge from the results of analysis, or that some samples would give clearcut indications of components of the patinas.

The bronzes chosen fall into two groups: central Italian, defined as the work of Giambologna and his immediate successor; northern Italian, a heterogeneous group of examples from Paduan, Mantuan, and Venetian Schools. These two groups are by no means exhaustive or comprehensive with respect to bronzes bearing organic patinas in the Metropolitan Museum.

The Giambologna group:

As has been recognized, the bronzes of Giambologna and his associates were generally coated with 'lacquer' or 'varnish' of an organic nature. Three color groups may be distinguished: possibly the commonest is a deep chestnut-brown; a more yellow-brown which can be startlingly golden and transparent; a deep red, verging on oxblood in the shadow. Subsequent tarnishing under the patina has darkened the metal which seems to have been polished originally.

Darkening of the organic patinas has no doubt greatly changed the appearance of these bronzes.

The Risen Christ (7; Met 09), St. John (8; Met 10), and St. Matthew (9; Met 11), are documented as having been executed by Antonio Susini for the Certosa di Galuzzo from models for at least the Christ by Giambologna. The technical evidence clearly supports this, as radiographs show very similar facture. All three have yellowish sandy cores, still intact, and similar alloys (Table 3). The patinas are identical to the naked eye, a rather dark brown. From the GC/MS data (Table 4) the patina of the Risen Christ seems to be a mixture of Venice turpentine, pine resin, and a drying oil, probably linseed. Drying oil and Venice turpentine were not detected in St. John, but the presence of a retene-like component strongly suggests that the pine resin was added as a dark pine pitch to tint the film brown. Unfortunately none of these ingredients was detected in St. Matthew, but if the three bronzes are considered as a unit, a plausible composition for the brown organic patina is: Venice turpentine, pine pitch, and linseed oil.

The Giambologna Pacing Horse (1; Met 01), has a rather fine brown patina, somewhat worn. GC/MS results indicate a triterpenoid resin, probably mastic, pine colophony, and linseed oil, a mixture similar to, but not identical with that found for the Certosa di Galuzzo group. Similar patinas may have been achieved in more than one way.

The GC/MS analyses of two other Giambologna bronzes is difficult to interpret. The Fortuna (10; Met 12), shows traces of an unspecified conifer resin and traces of oil, possible walnut. The Francesco di Medici (15; Met 18), despite magnificent reddish-brown patina showed only traces of an uncharacterized drying oil. This result may represent the effect of an inorganic pigment in rendering the medium difficult to analyse.

The Hermaphrodite (12; Met 14, Met 15), is a signed and dated (1639) work by Gian Francesco Susini, nephew of Antonio. It was made in two pieces: the base and the figure of Hermaphrodite. The patina is an identical dark brown in both pieces and taken together ought to provide a check for internal consistency for the analytical procedure. Unfortunately GC/MS analyses detected only a trace of bituminous material, possibly from a later retouch. The bituminous material was detected in only one of the four samples taken from this bronze and illustrates the serious difficulty in obtaining a representative sample.

The North Italian Group

Many North Italian bronzes have blackish, rather opaque patinas which frequently appear to be pigmented. They vary in reflectivity from matte to quite glossy. Several examples of these distinctly paint-like coatings were chosen.

The two earliest works are both probably from Venice: the Ascension of Elijah (3; Met 04) tondo and the Seated Hercules (4; Met 05), attributed to Camello. GC/MS results indicate that both contain a drying oil, walnut for the Hercules, and probably walnut for the Elijah. Both also showed the presence of conifer resin, which in the case of Hercules seemed to be larch.

Two later Venetian works, the tondo of Bernardo Soranzo (16; Met 19), signed by Andrea Spinelli in 1540 and the signed St. Sebastian (6; Met 08), of Alessandro Vittoria also showed the presence of drying oils by GC/MS analyses, of which only the linseed oil on the St. Sebastian was positively identified. They both showed the presence of conifer resin, the Bernardo Soranzo clearly being Venice turpentine.

It is interesting that the above four Venetian bronzes (probably from different workshops) all indicated the presence of conifer resin, which in at least two cases seemed to be larch. In none of the four examples was pine pitch detected despite their dark color. Although negative evidence for this type of analysis must be embraced cautiously, it is attractive to suggest that the source of the dark surface color arises from some sort of carbon pigment, which would not be detected by any analytical techniques employed in this work.

The Rider Surprised by a Snake (5, 5A; Met 06, Met 07), has been attributed to Francesco Sant' Agata and is certainly Paduan though influenced by Mantua. Both the separable rider and the horse were shown by GC/MS to have surfaces that contain linseed oil, mastic resin, and asphaltum, a composition quite different from the Venetian examples. The asphaltum probably supplies the deep brownish-black color.

The two pendant reliefs (Met 21, Met 22), the Arrest and Martyrdom of St. Daniel by the Paduan, Tiziano Aspetti appeared not to have patinas rich in organic material. GC/MS analyses indicated the presence of walnut oil in both but no resin was detected. Considering how matte the patinas appear, this result is not surprising. The color may come from a carbon pigment or possibly an inorganic pigment.

Finally the bust of Antoninus Pius (2; Met 02, Met 03), by the Mantuan Antico: The patina of this bronze has been shown by X-ray diffraction to contain copper oxides. GC/MS analyses of two samples from the surface failed to detect varnish ingredients. The appearance of the bronze suggests the presence of an organic material as vehicle or fixative for the colored surface material. As suggested for other examples suspected of substantial amounts of inorganic pigment, the medium may be rendered intractable to the extraction processes necessary for a successful analysis.

Considering the results from the Rider Surprised by the Snake in light of the results obtained from the Antoninus Pius, it is interesting that despite the stylistic and technical influence of Mantua on the Rider and the similar surface appearances, the composition of the patinas seem to be quite different; perhaps another illustration of the use of more than one method of obtaining similar surfaces.

Conclusions

1. All bronze surface samples examined showed the presence of organic material.
2. Appearance could not be used to predict the surface patina composition.
3. Serious problems were encountered in obtaining representative and/or replicate samples for the determination of surface patina components by GC/MS. Assays according to techniques that produce results with high confidence for easel and panel painted surfaces appear to be less reliable for bronze surfaces owing to the much more thinly applied and more completely oxidized material.
4. Greater weight should be given to positive GC/MS results in suggesting bronze patina components than to negative results since, for any given sample, degradation may have reduced the analysable (extractable) material below the threshold of detection.
5. Inorganic pigments, when present, are detectable by XRD.
6. Bronze composition may be a promising indication of geographic or workshop origin, but many more examples must be assayed.

References

1. C. Avery and A. Radcliffe (Eds), Giambologna 1529 - 1608: Sculptor to the Medici, exhibition catalog, (Edinburgh: Royal Scottish Museum; London: Victoria and Albert Museum, 1978).
2. C. Avery, Giambologna: the Complete Sculpture, (Oxford: Oxford University Press, 1987).
3. J. D. Draper, "Andrea Riccio and his Colleagues in the Untermeyer Collection," Apollo, (1978): 107.
4. J. Martineau and C. Hope (eds), The Genius of Venice 1500 - 1600, exhibition catalog, (London: Royal Academy of Arts, 1983).
5. O. Raggio, "Tiziano Aspetti's Reliefs with Scenes of the Martyrdom of St. Daniel of Padua," Metropolitan Museum Journal, 16 (1981): 131-146.
6. Natur und Antike in der Renaissance, exhibition catalog, (Frankfurt am Main: Liebieghaus Museum alter Plastik, 1985).
7. W. S. Sheard, Antiquity in the Renaissance, exhibition catalog, (Northampton, Mass: Smith College Museum of Art, 1979).
8. A. P. Darr (Ed), Italian High Renaissance Sculpture in the Time of Donatello, exhibition catalog, (Detroit: Detroit Institute of Fine Arts, 1985).
9. J. S. Mills and R. White, The Organic Chemistry of Museum Objects, (London: Butterworths, 1987) Ch 12.
10. R. White, "Brown and Black Organic Glazes, Pigments and Paints," National Gallery Technical Bulletin 10 (1986): 58-71.
11. N. Indictor, and R. J. Koestler, "The Identification and Characterization of Metal Wrapping in Historic Textiles Using Microscopy and Energy Dispersive X-ray Spectrometry - Problems Associated with Identification and Characterization," Scanning Electron Microscopy 2 (1986): 491-497.
12. M. Ballard, R.J. Koestler, and N. Indictor, "Weighted Silks Observed with Scanning Electron Microscopy - Energy Dispersive X-ray Spectrometry (SEM-EDS)," Scanning Electron Microscopy 2 (1986): 499-506.

Table 1. BRONZES EXAMINED.

Sample Designation (MMA) (Nat. Gal.)	MMA Accession No.	Sculptor, Title	Color (Visual)	Ref.
1. Met 01	24.212.23	Giambologna, Pacing Horse	Brown	1, #154
2. Met 02	65.202	Antico, Antoninus Pius	Black	6, #24
Met 03	65.202	Antico, Antoninus Pius	Black	
3. Met 04	17.190.1405	Vanetian, Elijah Tondo	Black	*
4. Met 05	64.304.2	Camelio, Hercules	Black	6, #15
5. Met 06	64.101.1419	Rider on Horse (Horse)	Br. Black	5, figs. 14, 15**
5A Met 07	64.101.1419	Rider on Horse (Rider)	Br. Black	
6. Met 08	40.24	Vittoria, S. Sebastian	Black	4
7. Met 09	63.39	Giambologna, Christ	Dk. Brown	1, #12; 2, #101
8. Met 10	57.136.1	Giambologna, St. John	Dk. Brown	1, #113
9. Met 11	57.136.2	Giambologna, St. Matthew	Dk. Brown	1, #114
10. Met 12	24.212.5	Giambologna, Fortuna	Dk. Brown	1, #14; 2, #57
11. Met 13	32.100.183	Giambologna, Venus & Cupid	Dk. Brown	1, #10
12. Met 14	1977.339	G.F. Susini, Hermaphrodite	Dk. Brown	1, #189
13. Met 15	1977.339	G.F. Susini, Hermaphrodite	Dk. Brown	
14. Met 16	64.304.1	Bellano, David & Goliath	Dk. Brown	8, #82
Met 17	64.304.1	Bellano, David & Goliath	Dk. Brown	
15. Met 18	1983.450	Giambologna, Francesco I Medici	Red	2, #36
16. Met 19	51.119	Spinelli, Bernardo Soranzo	Black	***
-- Met 20	1970.264.1	San Daniele (Nailed)	Black	5
-- Met 21	1970.264.2	San Daniele (Dragged)	Black	

*Attributed to the Barbarigo Master.

**As Francesco da Sant'Agata

***A portrait medalion of Bernardo Soranzo signed and dated 1540 by Andrea Spinelli

Table 2. ANALYSES PERFORMED ON SAMPLES.

Sample Taken From	Sample Treatment	Analytical Tool	Detectable Matter
Patina	Ether/Benzene extract, methylated	GC/MS ^a	Waxes, shellacs, resins, etc.
Patina	Extract residue, saponified, methylated	GC/MS ^a	Drying oils, bitumens, etc.
Patina	Untreated	XRD ^b	Pigments, inorganic substances.
Patina	Carbon coated	EDS ^b	Inorganic elements
Metal	Untreated	EDS ^b	Bronze elemental composition
--	--	Visual obs ^b	Color

^aNational Gallery Scientific Department, London.^bMMA Objects Conservation Department, NY.

Table 3. GC/MS Results Summarized

Nat. Gal. Designation	MMA Access. No.	Sample Treatment Prior to GC/MS	
Met 01	24.212.23	conifer resin ^c (probably pine); triterpenoid resin ^e (probably mastic)	drying oil ^{d,x}
Met 02*	65.202	ceresine ^f ; bitumen ^g	
Met 03	65.202	ceresine ^f ; bitumen ^g	shellac ^h
Met 04*	17.190.1405		drying oil ^{d,y} ; shellac ^h
Met 05*	64.304.2		conifer resin ^c (probably pine) drying oil ^{d,y} ; conifer resin ^{c,i,j} (possibly larch?)
Met 06	64.101.1419	mastic resin ^{e,h} ; bitumen ^g	drying oil ^{d,x}
Met 07	64.101.1419	mastic resin ^{e,h} ; bitumen ^g	drying oil ^{d,x}
Met 08*	40.24	conifer resin ⁱ (probably pine)	drying oil ^{d,x}
Met 09	63.39	larch resin ^{c,i,k}	drying oil ^d ; shellac ^m
Met 10*	57.136.1	conifer resin/pitch ^{c,i,o} ; beeswax	shellac ⁿ
Met 11*	57.136.2	beeswax ^{f,p,q} ; fats ^p	
Met 12*	24.212.5		drying oil ^{d,y} ; conifer resin ^r
Met 13	32.100.183		non-drying fats ^s
Met 14*	1977.339		non-drying fats ^s ; shellac ⁿ
Met 15*	1977.339	beeswax ^t ; bitumen ^g	
Met 16	64.304.1		non-drying fats ^s
Met 17	64.304.1		non-drying fats ^s ; shellac ^{m,n}
Met 18	1983.450		non-drying fats ^s ; drying oil ^{d,u}
Met 19	51.119	ceresine ^f ; larch resin ^{c,i,k}	drying oil ^d
Met 20	1970.264.1	beeswax ^t	drying oil ^d
Met 21	1970.264.2	beeswax ^t	drying oil ^d

*Replicate analyses. ^aEther/benzene extr., methylated. ^bResidue from ether/benzene extr. sapon, acidified, methylated. ^c(m/z=239,314: methyldehydroabietate). ^d(m/z=55,185: methyl-azelate; 74,270: methylpalmitate; 74,298: methylstearate). ^e(m/z=203,328: triterpenoid keto acid methyl ester). ^f(m/z=57). ^g(m/z=191). ^h(m/z=189,468: moronic ester). ⁱ(m/z=253,328: methyl-7-oxodehydroabietate). ^j(m/z=69,81,109: larixol?). ^k(m/z=69,81,109,286: larixol). ^m(m/z=308). ⁿ(m/z=278). ^o(m/z=223,238: retene). ^p(after sapon., acidification, methylation). ^q(m/z=74). ^r(m/z=239). ^s(m/z=74,270: methylpalmitate; 74,298: methylstearate). ^t(brief extract, benzene, gc anal. only). ^u(m/z=149: methylphthalate [alkyd or plasticiser?]). ^x(linseed). ^y(walnut).

Table 4. METAL COMPOSITION OF BRONZES - EDS ANALYSES

Sample No.	Element % ^a							
(MMA)	Fe	Cu	Ag	Sn	Pb	Zn	Sb	Si
1.	0.32	93.39	-	5.65	2.77	-	-	-
2.	N.D. ^b							
3.	0.38	92.87	-	-	0.81	5.98	-	-
4.	0.40	92.07	-	2.05	5.89	-	2.25	-
5.	0.19	99.99	0.38	4.38	1.77	-	-	-
5A.	0.71	94.74	-	2.84	2.31	-	-	-
6.	0.52	83.79	-	8.94	9.19	-	-	-
7.	0.13	87.17	-	4.26	10.54	-	-	-
8.	-	82.32	-	2.92	17.62	-	-	-
9.	0.23	90.61	-	2.29	8.42	-	-	-
10.	0.90	59.25	-	3.27	41.64	-	-	-
11.	0.51	80.71	-	4.13	16.27	1.19	-	-
12.	0.10	93.16	-	6.42	1.15	-	-	0.14
13.	-	91.23	-	7.30	2.66	-	-	0.15
14.	0.37	81.21	0.40	0.77	17.89	-	2.32	0.07
15.	-	87.93	-	11.12	2.49	-	-	0.16
16.	0.52	71.86	-	1.88	27.11	0.83	1.24	- [Ni 0.48]

^aData obtained by ASAP routine, not normalized. Range (total % for each sample): 100.04 - 106.72 (103±3). To normalize: divide each value by the sum of each row in which the value occurs.

^bN.D.= No data.

Table 5. EDS ANALYSES OF PATINA LAYERS

Sample No. (MMA)	Element % ^a										Other Elem. ^c
	Fe	Cu	Zn	Si	Ca	S	Al	Mg	K	Cl	
1.	N.D. ^b										
2.	(+)	++	-	(+)	+	+	-	-	(+)	+	-
3.	(+)	+	++	(+)	++	(+)	(+)	(+)	(+)	(+)	Na, P
4.	(+)	++	+	+	+	++	(+)	(+)	(+)	-	P
5.	N.D.										
6.	(+)	+	+	+	++	+	(+)	(+)	(+)	(+)	P
7.	N.D.										
8.	(+)	+	-	++	++	+	(+)	(+)	(+)	(+)	-
9.	(+)	++	-	++	+	+	(+)	-	(+)	(+)	-
10.	(+)	++	-	(+)	(+)	+	(+)	-	(+)	(+)	Pb(++), Ag
11.	N.D.										
12.	(+)	++	-	(+)	(+)	+	(+)	-	(+)	(+)	P
13.	(+)	++	-	+	(+)	+	(+)	-	(+)	(+)	-
14.	N.D.										
15.	(+)	+	+	+	++	++	(+)	(+)	(+)	(+)	-
16.	(+)	++	-	(+)	+	+	(+)	(+)	(+)	(+)	P
20. ^d	(+)	++	++	+	+	+	(+)	-	(+)	(+)	Ti
21. ^d	(+)	++	-	+	++	+	(+)	(+)	(+)	(+)	Ti

^aData obtained by ASAP routine, normalized; normalization factors (total %+100 for each sample): 0.7±0.1. Elements of atomic no. > 11. (+) = < ca 10%; + = > ca 10%; ++ = > ca 20%; - = not detected.

^bN.D.= No data. ^cTrace, unless otherwise indicated. ^dNational Gallery Designation



Working Group 17

Lighting and Climate Control

Eclairage et contrôle du climat



ABSTRACT

The purpose of this work was to study necessary conditions for setting up a satisfactory system for humidity control of showcases by the use of saturated salt solutions. Different systems of salts and containers for the solutions have been tested in the laboratory. The experiments show that creeping of salts up the walls of the containers may be avoided by the right choice of salts and container materials. Laboratory tests and more than 30 years of experience in museum show that humidity control of showcases by salt solutions can offer an easy and cheap alternative to other humidity control systems.

KEYWORDS

Humidity control, showcases, salt solutions, passive system.

SATURATED SALT SOLUTIONS FOR HUMIDITY CONTROL OF SHOWCASES - CONDITIONS FOR A SUCCESSFUL SYSTEM

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Introduction

In museum collections at fairly stable temperatures, keeping the relative humidity (RH) constant will ensure that climate conditions and moisture content of objects also remain stable. Stabilization of RH inside showcases can be obtained in different ways. One way of doing this, to which little attention has been paid, is by use of saturated salt solutions or salt slurries. How to set up such a RH control system and how this system functions have been described earlier (1). More than 30 years of experience with salt solution control of showcases in the Viking Ship Museum in Oslo, Norway, shows that a saturated solution of calcium nitrate tetrahydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, provides a satisfactory stabilization of the RH at around 50-60% in the wet season as well as in the dry season.

The advantages of using saturated salt solutions for the stabilization of showcases are that the system is cheap and easy to set up, and that little maintenance is needed to keep the system going.

One particular argument which is often given against the use of salt solutions for this purpose, is the tendency of the salt crystals to "creep" up the walls and over the edges of the container (2). The behaviour of different salts in containers of different materials and shapes is reported in this work.

Also, the fear of salt crystals being scattered around in the showcase, speeding up the corrosion process, seems unfounded after salt solutions have been used more than 30 years in the Viking Ship Museum, without any visible corrosion on the iron objects.

"Creeping" of salts

Despite the fact that salt creeping seems to be the main reason why this type of humidity control is not more widely used in museums, creeping of salts never has been a problem in the Viking Ship Museum. It therefore seemed to be of interest to look more closely into the behavior of different salts, especially those which have been tried out for this purpose (3,4). Further more, the degree to which this effect is influenced by different materials and shapes of container in which the solutions are kept, has been studied.

From chemistry it is known that if a solution of a salt in water is placed in a closed room, it will establish a constant RH in the air above the solution. The RH is somewhat dependent on temperature, but within the temperature ranges which are usually found in museums, this can be disregarded. Outlines of relative humidities established by different salt solutions can be looked up in tables (5).

The literature gives little information about different salts which have been used for humidity control. Besides the salt which is used in the Viking Ship Museum in Oslo, i.e. calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), also sodium bromide (NaBr) (3), and magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (4) are reported in the literature used for this purpose. The choice of the salts which have been tested and compared in this work, comprises the three above mentioned, which have been used for climate control. Also sodium sesquicarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3$) has been included as a test sample, as this salt is known from metal conservation to creep drastically in plastic boxes.

The experiments have been carried out in containers of four different materials, i.e. stainless steel, polyethylene (PE), styreneacrylnitril (SAN), and polyvinylchloride (PVC). These

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CONTAINER MATERIALS

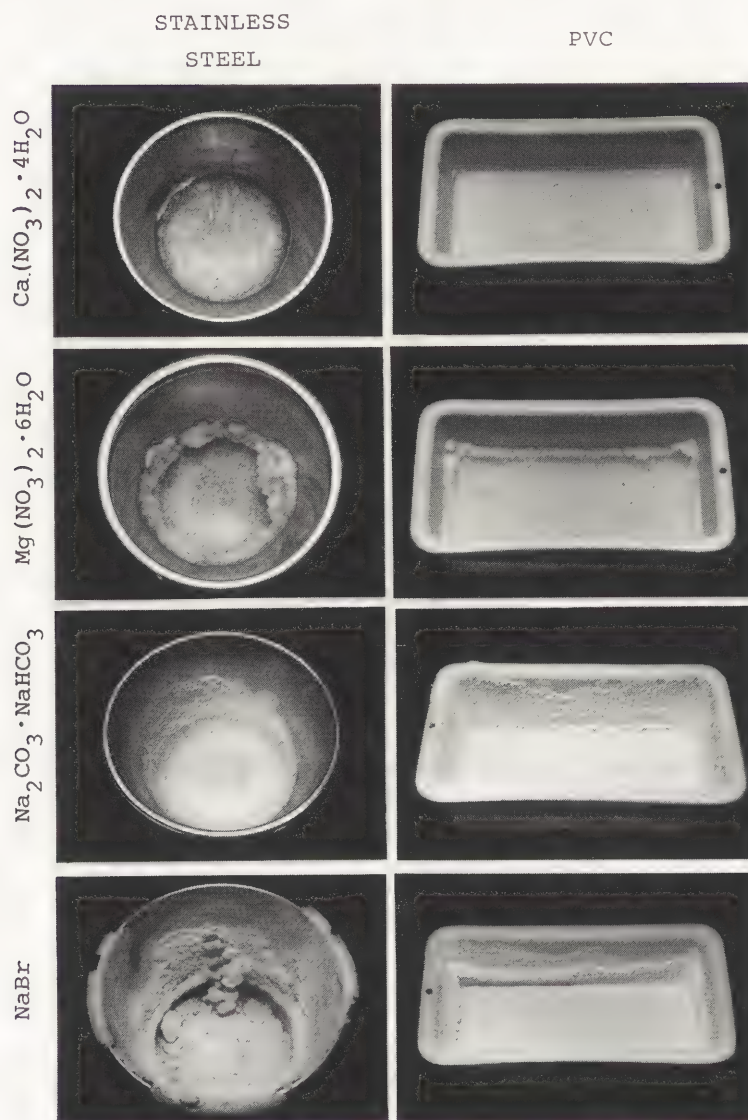


Fig. 1a The photographs show how different salts react in containers of different materials. The horizontal rows correspond to different salts, the vertical columns to the container materials.

materials are chosen partly because they are found to be easy to handle and well suited for containers in showcases and partly because they have different chemical properties. Glass containers have not been tested as these are found to be too fragile and inconvenient to use inside showcases.

The tendency of the salts to creep up the walls of the containers have been studied in the laboratory. The salt solutions have been prepared in the same way as for museum showcases, i.e. the salts have been dissolved in water until saturation of the solutions (ca. 500 g salt per 100 cc water at room temperature), and then some additional solid salt has been added. The surplus of salt assures that the solution stays saturated even if the water content is increased by absorption of water vapour from the air. The absorption and evaporation of water from the solutions has been carried out at ordinary room temperature without any attempt to speed up the process in an artificial way.

As expected, the results show that some salts creep a lot, while others have little or practically no tendency to creep. The results from the creeping experiments of the salts are summarized in table I, while fig. 1 shows how the various salts behave in the different containers. It also seems evident from fig. 1 that some of the salts show the same tendency to creep regardless of the material of the container, while for other salts the creeping is dependent on the container material.

CONTAINER MATERIALS

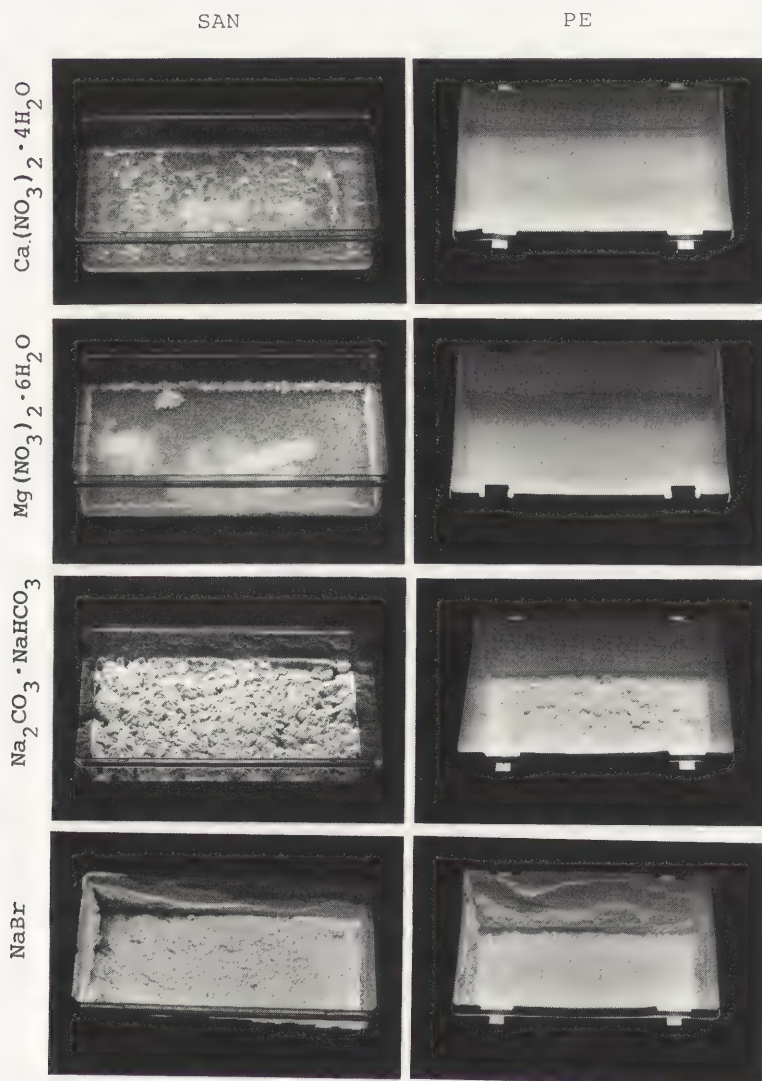


Fig. 1b The photographs show how different salts react in containers of different materials. The horizontal rows correspond to different salts, the vertical columns to the container materials.

As may be seen from fig. 1 and table I, the use of calcium nitrate tetrahydrate causes no trouble when used in any of the tested containers, while sodium bromide causes great problems in all the containers. As for magnesium nitrate hexahydrate and for sodium sesquicarbonate the tendency of creeping is dependent on the material of the container.

The creeping of salts in saturated solutions is determined mainly by two factors, i.e. by the way in which the salt crystallizes and by the surface tensions and the interfacial tension at the boundary between the salt solution and the container. In order to avoid creeping it is an advantage to use salts which dissolve easily in water and possibly in supersaturated solutions. By choice of containers it is important that the surface is smooth. Metal containers, although they may have a polished surface and are easy to handle, should not be recommended, as saturated salt solutions sooner or later will attack the metal. Organic polymer materials, such as polyethylene, will usually be a better choice.

salts	container materials			
	stainless steel	PVC	SAN	PE
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	0	0	0	0
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	++	+	+	0
$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3$	++	+++	0	0
NaBr	+++	+++	+++	+++

Table I. The tendency of salts to creep up the walls of containers of different materials. 0 corresponds to no creeping, while +, ++ and +++ indicate from little to vigorous creeping of the salts.

Shapes and sizes of containers

Questions have been put forward as to what effect the shape of the container has on the creeping of salts up the walls of the container.

Salt creeping has therefore been tested in containers of different shapes. The containers which have been tested have either a circular bottom and sloping walls (ca. 10-20°) or square bottoms and perpendicular walls. Containers of metal (i.e. stainless steel) and plastic (i.e. polypropylene) have been used in the experiments.

By comparison of results from tests carried out in different containers, the shapes of the containers, as mentioned above, do not seem to be of essential importance. As long as the salt and the container material are the same, the observed creeping seems to be equal in containers having vertical or sloping walls.

In order to achieve a humidity control of showcases with as little maintenance as possible, it is necessary that the volume of the salt solution is large enough to provide enough water vapour in a climatically dry period. Furthermore the volume of the container must be large enough to hold all the water which is absorbed from the air in a particularly wet season. The amount of water evaporated or absorbed will be dependent on the difference in RH outside and inside the showcase, and also on how impervious the showcase is to water vapour.

Evaporation and absorption of water vapour takes place from the surface of the salt solution. Therefore not only the volume but also the surface area of the salt solution will influence the humidity control process. The larger the surface, the faster a constant RH, will be established by evaporation or absorption. However, even for a comparatively small surface an equilibrium giving a constant RH can be obtained, but the time needed will be longer. When the showcase is poorly sealed untight and the fluctuations in the RH outside the showcase are large, there may be difficulties in establishing an equilibrium and obtaining a constant RH if the surface area of the salt solution is too small compared to the volume of the showcase.

Fig. 2 shows the results from experiments on humidity control with salt solutions having different surface area. The tests have been carried out in well sealed test cases of polymethyl methacrylate (Perspex) in the laboratory. The left part of the curve shows the stable RH in the test cases (56 % RH, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$). The test case is then humidified for 18 hours (ca. 84% RH) before the salt solutions are inserted. For a salt solution having a surface area of 0.5 m² per m³ air (solid line) the RH is re-established in about 14 hours. A salt solution with a surface area of 0.03 m² per m³ air (stippled line) needs about 3 days for re-establishing the RH. In both cases a constant RH is eventually obtained when enough time is given to establish the equilibrium.

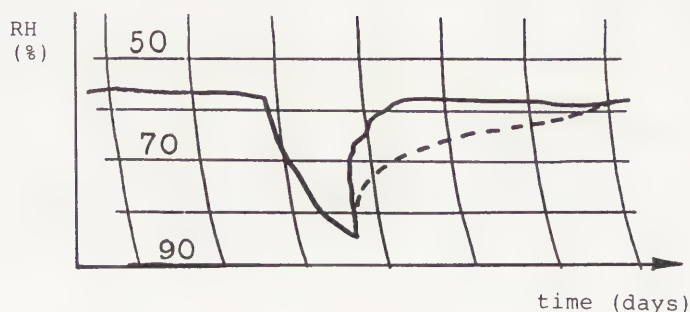


Fig. 2 A section of recordings from thermohygrographs, showing how the rate of re-establishment of RH is dependent on the surface area of the salt solution. Solid line : surface area 0.5 m² pr. m³ air; stippled line : surface area 0.03 m² pr. m³ air.

Conclusion

The importance of controlling relative humidity (RH) in museum collections is gradually gaining acceptance in most museums. Large and costly air conditioning systems are introduced for control of larger areas. The use of silica gel is well-known for control of smaller volumes, such as showcases. The use of saturated salt solutions or salt slurries for control of RH is, however, not widely spread nor well-known.

The general argument against the use of salt solutions, namely the problem which exists when salt crystals "creep" up the walls of the container and over the edges, has never been any problem in the showcases at the Viking Ship Museum in Oslo, Norway, where salt solution systems for humidity control have been more than 30 years in operation.

Based on experiments with different salts and different container materials, this work shows that the tendency for salts to creep up the walls of the containers is partly due to the properties of the salt and partly to the material of the container. Although many salt/container systems result in a serious creeping, it is possible to put up systems where creeping does not make any problem.

In order to establish and to keep a constant RH inside a showcase it is important to have a sufficiently large container to hold a variable volume of solution, a sufficiently large surface area of the solution for absorption and evaporation of water vapour, and enough salt to keep the solution constantly saturated. No general rules can tell what will be sufficient, as this will depend on the air tightness of the showcase and the exchange of air and water vapour between the outside and the inside of the showcase.

The surface area of the salt solution at the Viking Ship Museum in Oslo is 0.2 m² per m³ of air in the showcases. This is sufficient to keep a satisfactory RH between 50-60 % throughout the year, even when the RH in the museum exhibitions outside the showcases may fluctuate between 20-80 %.

The maintenance of this system amounts to addition of water usually once a year in the dry season. The fact that this system works so well with minimum maintenance, is partly due to the fact that the RH wanted in the showcases, lies somewhere between the upper limit of the RH in the wet season and the lower limit of the RH in the dry season in the museum building. This means that the salt solution absorbs water during the wet season and gives off water during the dry season, i.e. a long term stabilisation of RH.

In locations where the RH which is wanted in the showcase, is constantly far below that of the air outside the showcase a continuous deshumidification is needed. For a salt solution system this will result in a continuous absorption of water vapour from the air and a constant increase of the solution volume in the container. Somewhat more maintenance may then be needed in order to keep the solution saturated, and a surplus of the solution may have to be removed.

In locations where the air in the showcase is constantly too dry for a satisfactory maintenance of the collection, the salt solution will work as a humidification system. The amount of water which evaporates from the solution, will have to be added to ensure that the salt never becomes dry.

The experiences from the Viking Ship Museum show that the great advantage of the saturated salt solution system for humidity control lies in the fact that it is a cheap system which is easy to set up and free from break-downs, it is independent of electrical supply and little maintenance is needed.

NOTES

1. E.E. Astrup, "Is it Worth-While Re-Looking at Salt Solutions as Buffers for Humidity Control of Showcases?", ICOM Committee for Conservation: 8th Triennial Meeting, K. Grimstad ed., Sydney (1987) 853-858.
2. G. Thomson, The Museum Environment (London: Butterworths, 1986), 113-114.
3. T. Padfield, "Control of Relative Humidity and Air Pollution in Showcase and Picture Frames", SIC, no. 11 (1966): 8-30.
4. S.P. Sack, "A Case Study of Humidity Control", Brooklyn Mus. Art. Rep., no. 5 (1963-64): 99-103.
5. Handbook of Chemistry and Physics (Ohio: The Chemical Rubber Co.)

ABSTRACT

The 50/150 lux recommendations were established by Thomson on the basis of visibility. We see most of what there is to see in this range, but we see better and differently with brighter light. Thus "best" lighting will always involve opinion, and not just the conservator's. What the conservator must provide are specific rates of fading, not vague, often false generalizations. Lightfastness data has been available for decades, but conservation has ignored it. CCI has reviewed this literature, and developed a slide rule to calculate fading, once the international lightfastness rating is known. Summaries on historic colorants are under way for use with the slide rule. Less technical guidelines are being drafted based on Feller's broad but specific categories: fugitive, intermediate, durable, and permanent.

KEYWORDS

Light, standards, fading, visibility

TOWARDS SPECIFIC LIGHTING GUIDELINES

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Introduction

"The Japanese report (of 1930)... concluded that the best level of daylight is about 50-70 lux for Western oil paintings and 100-120 lux for Japanese paintings. (Artificial) lighting to be found in French museums...an average of 75 lux (1934).

The levels recommended...are neither drastic nor revolutionary, but attempt a synthesis between new ideas and established practice...

Most museum objects, including oil and tempera paintings...Not more than 150 lux. Specially sensitive objects (watercolours, textiles, tapestries, etc.)...Not more than 50 lux"

Garry Thomson 1961¹

"The 150/50 lux recommendations ... are not based on numerical formulae, but are an attempt to balance the need for good viewing against the need for good conservation. These levels can therefore be contested as soon as new information is presented concerning either (a) the relation between light levels and viewing, and (b) rates of damage by light in museums."

Garry Thomson, ICOM, 1972²

I want to show two things:

- * *Scientific data on visibility can never decide recommendations because it only confirms what our eye told us already: there is no simple optimum.*
- * *Information on rates of damage has been available a long time, but conservation has avoided it. It is not simple, but it is time to make use of it.*

The light recommendations started reasonably, but they hardened into rules. People forgot their origin. It got to the point that even Thomson, who chose the numbers, justified them in his book by a list of conforming institutions³ (including CCI), but they did so because he did so. This is not to say the numbers are unreasonable: Thomson showed this range had been acceptable for electric lighting everywhere before the 60's.¹ Notice that they began as maximum recommended, but like speed limits, became the norm. Unfortunately, the reason for the 150 (now 200) lux group has never been clear, if it is true that 50 lux "gives satisfactory lighting even of small objects with low contrast."⁴ Were oil paintings three times less sensitive, or three times darker?

As Thomson said above, the issues are visibility and rates of damage. In his book³, as in our *Technical Bulletin*⁵ and many general articles, these topics get about 10% of the text, and are vague. The rest is physics, colorimetry, and lighting fixtures, the easy stuff. Although the museum community likes us to provide this information, I think we are forgetting the central issues - visibility and rate of deterioration.

Visibility

In 1972, Bromelle⁶ introduced some visibility data to conservation. He pointed out that you get much less than twice the acuity for twice the light. Unfortunately, one can defend 1000 lux even better than 100 lux with this argument. As Thomson noted later: "the luminance scale becomes very elastic and loses usefulness, and we move yet further from being able to make use of visual performance data." ⁷

There is only one obvious transition in our vision. Between 0.01 lux and 3 lux, our eye converts from colourless night vision to colour vision (for typical surfaces)⁸. Verriest et al⁹ and Crawford¹⁰ showed we can discriminate colours as well as possible by 10-20 lux (typical colours). The data on acuity (fine detail) is not so simple. Although most detail is visible by 10-20 lux,¹¹ fine detail is progressively more visible with more light, right up to

full daylight. Therefore, we cannot say 50 lux provides "complete" visibility. We can say that at 50 lux most bright things are clearly visible, that at 150 lux most dark objects are clearly visible, and that people over 50 may need more to see as well. These are the conclusions Boyce draws in a recent and readable review.¹¹

Ikeda et al¹⁰ recently measured the phenomenon whereby bright light makes coloured surfaces look brighter relative to a grey scale. Aesthetically, this is rather a profound effect. The authors state that with more light, colours appear

"more vivid and stronger, and consequently objects of high saturation gain in brightness more than those of less saturation" ¹⁰

At very high levels the effect may be as the artist Rothko described:

"if there is too much light the colour in the picture is washed out." ¹²

Recently, Loe¹³ studied peoples' likes and dislikes in an experimental picture gallery, and concluded 200 lux was best. Thomson changed his 150 lux recommendation to 200 lux, largely because of this study. But the conclusion was partly opinion, dependent on the curve chosen to fit the scattered data, and where on the knee of the curve one says "Aha, the best!" My opinion is that the data on people's judgement of the "quality" of lighting shows little improvement between 50 lux and 400 lux. So, both the data on how our eye sees, and this data on people's judgement of lighting, cannot get us away from opinion.

Overall, two general facts about visibility emerge:

- * We see most of what there is to see by 50 lux. This has been the standard argument of conservation.
- * We see objects not only slightly better, but differently with more light (such as the brightness of colours).

Conservation must not deny that difference, or trivialize it. *Our job is to explicitly predict the cost in deterioration. Other professions in the museum must be involved in deciding whether or not to pay that price.*

Rate of Deterioration

Throughout the last fifty years of museology, individuals have measured the rate of deterioration by light, and published the results. Somehow, these never influenced lighting recommendations which were based on visibility alone. Museums mistakenly think that "conservation lighting" solves the ethical problems of display. It does not. The artifacts are fading. The museum needs to know how fast, so it can "ration" fugitive colours.

In 1950, Stromberg¹⁴ showed results at the ICOM Committee on Museum's Displays from many tests, such as: effect of light source on Swedish lightfastness standards I to VIII (started 1937 for Nordiska Museet) and tests on "old Swedish peasant weaving and embroidery" (started 1932). She concluded:

"Most old time colours possess a fastness only equal to (Swedish standards) No.'s II to IV....After three years, No. IV exposed to (incandescent) artificial light had just started to fade"

These were not vague statements about sensitivity: three years will start to fade "most old time colours" (historic dyes) even at low museum light levels (25 Watt lamp at 0.5 m, so probably about 100-200 lux).

Stromberg also carried out tests on 30 eighteenth century samples, using the German/British lightfastness standards of the 1950's. These standards became the international standards of today, ISO 1 to 8. Therefore these tests have particular value to us now, because the standards are recognizable, and because the samples were authentic.

In a 1953 report for the Metropolitan Museum, Harrison,¹⁵ a lighting engineer, used Stromberg's daylight data in his conclusions. Unfortunately, his estimate for improvement with low UV sources was exaggerated, (he ignored Stromberg's incandescent test.) He did however, make the point that even good dyes can fade "definitely" after a decade or two in some of the museum's galleries. Harrison's wavelength damage factors, in fact NBS factors, were remembered instead of his fading estimates. *It has always been more acceptable to say: this light source is less damaging than that, rather than say absolutely, the safest light will fade this colour in a few years.*

Ironically, the NBS wavelength damage factors¹⁶ were an example of muddled extrapolation that I wish to avoid. D. B. Judd, an eminent scientist in colour vision, seems to have been asked to say something about an area outside his expertise. He based his calculations on a small study¹⁷ of paper "strength", not colour fading. He referenced two other articles in support of the data. These turn out to be: 1) a good but irrelevant study of cellulose¹⁸ and 2) un referenced graphs from a medical text¹⁹ one could kindly call eccentric. In final form, the "data" is extrapolated to a long table with many more wavelengths and significant digits than the original data. It predicts enormous improvements with UV filters, but Harrison himself quoted several textile studies that showed UV filters made little difference to colour fading^{20 21}. For some reason, he put his faith in the NBS table instead. Fortunately, most later researchers realized that the NBS damage factors had little to do with fading of colour, although the concept does have application to UV damage such as strength loss, chalking, etc.²²

Feller's review articles^{23 24} of the 60's gave many examples of rate of damage. His *Museum* article²⁴ is still the best introduction to the subject. He concluded:

" Essential facts and principles have been known for a long time. There is a need in the future...to establish more precisely the list of susceptible materials...and to gain some measure of the amount of exposure necessary to cause specific amounts of these changes. "

The conclusions otherwise were the same general advice as before: be careful. The reader could easily forget just how fast some colours fade. Feller's later studies, such as vermilion²⁵ and Japanese prints²⁶ indeed answered "the amount of exposure necessary" but these articles are not widely distributed.

In 1966, Padfield and Landi²⁷ published an article important not only for the data, which was not really a surprise, but for its clear conclusions:

" Fifty years of permanent exhibition in the dimmest tolerable conditions would destroy the yellow natural dyes and the red dye-woods and...
no valuable textile in good condition should be permanently displayed unless all the dyes are known to have a light-fastness above 6.
The exact colours of dyes should be recorded before they are displayed."

So, through the 50's and 60's, many good articles appeared on rate of deterioration, but none of it influenced recommendations to the museum world. More studies appeared in the 70's, with a similar fate. Why? Perhaps it was too complicated.

One reason was that the most influential writer, Thomson, didn't believe that the data from 30,000-100,000 lux tests could be used to predict what would happen at lower light levels. "Accelerated tests usually distort results beyond usefulness."²⁸ Certainly, accelerated tests using high temperature have had very mixed success, but both Feller and Padfield and Landi had found articles that supported "reciprocity", i.e. high intensity data did predict what happened at lower intensities.^{20 29 30} Others have appeared.^{31 32} Thomson also thought that the data given in terms of lightfastness standards was unusable since "Attempts have been made to measure how much light exposure is required to fade the standards. They have met with little success."³³ He refers to the early work of Rawland³⁴, which was certainly pessimistic, even the industrial literature then was divided.³⁵ Later work however, along with Rawland's, shows a usable consistency, (though not perfect). Even studies with fluorescent lamps can be fitted in, using McLaren's data on spectral effects. Others have appeared. I have published a review and chart of much of this data,²² and a more detailed description is in preparation³⁶. Overall, most of the data agrees quite well, *especially the fugitive materials that are most at risk.*

Of course, only studies of the artifacts themselves in low light levels will establish the accuracy of any predictions. Thomson himself initiated the most sophisticated long term study of this kind at the National Gallery, London.³⁷ Overall, though, it is clear to me that the predictions agree very well with both museum experience and general experience with particular colours. Further study will improve our calculations, but it will not radically change them.

CCI developed a Light Damage Slide Rule based on the available data, available for \$20³⁸. It is not meant to be a very precise tool. It provides a good estimate of whether fading will start or finish in days, years, decades or centuries. It shows quickly the benefits of reduced light intensity and reduced exposure time. Summaries of relevant ISO ratings for dyes and pigments to be used with the slide rule are in preparation. Generalizations such as given below can be plugged in immediately.

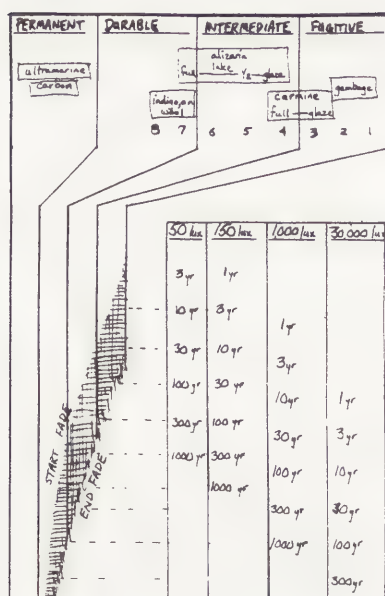


Fig. 1

Draft of a light damage chart for use in the CCI lighting guidelines. It provides a simpler level of explanation than the CCI slide rule.

The slide rule is still a bit technical, so I am also writing general guidelines.³⁹ These use Fellers three broad categories: fugitive (ISO 1-3), intermediate (ISO 4-6), durable (ISO 7 and above, but still affected). The fourth category, permanent, means permanent to light alone. Diagrams will allow readers to estimate rate of damage for each category (Fig. 1). The categories conveniently allow practical summaries:

(Assume good UV filters)

- * Most historic natural dyes and lake pigments, most plant and animal colours, fall in the fugitive category. These exist in new items and old, because books were closed, objects in storage etc.
- * Important exceptions: indigo and madder (alizarin) are durable on wool (just), but intermediate on silk, fugitive on cotton. Structural colours (e.g. iridescence) are durable.
- * All the important brilliant red pigments, carmine, madder lake, and alizarin lake, fall in the intermediate range, although carmine falls to fugitive in thin colour, alizarin lake makes durable at full strength. These are the colours we see at all stages of loss in figurative painting of the last few centuries. How fast do we want to use the remainder?
- * Top quality modern palettes and carbon inks are durable to permanent. Several hundred lux for several centuries will only just start to fade the weakest. Paints with durable and permanent pigments chalk long before they fade if there is UV present.
- * Gloss damage and chalking are essentially due to UV. Outdoors, most media are fugitive to intermediate. With UV filtration of ordinary glass, most are intermediate, under UV filters, virtually all become durable.

Conclusions

CCI lighting guidelines will explain the issues, rather than set rules. Other institutions can set "standards" that incorporate factors we cannot presume to tell them, such as: how long should the artifact last, how important are the aesthetic improvements with more light, what was the artists intent? Since most museums have incorporated preservation as part of policy; and since professional museum staff recognize conservation issues, conservators could drop the role of "lighting police" and instead become expert counsel, if they are expert. The museum consensus, or the artist's, or the tribal owners, may prefer a short effective life to a long shadowy one, but the decision should be conscious, not default. Some differences from current practice will emerge:

- * Current generalizations about media are wrong: paper and textile artifacts are not necessarily more sensitive than oil and paintings. Most paper itself (not tinting) is at least intermediate, much of it durable to light⁴⁰ (UV filtered) and many images on paper are durable or permanent (carbon, metal point, earth pigments, black and white photographs). On the other hand, oil paintings, watercolours, and furniture all may contain fugitive colorants. Generalizations should apply either to colorants, or to classes of object with common colorants. For example, watercolours or oil paintings with unknown palettes probably have at least one fugitive colorant and several intermediate. On the other hand both a watercolour on rag and an oil painting, with good palettes such as Winsor and Newton's "select list" are durable to permanent.
- * Institutions must deal explicitly with the short life of fugitive colorants. Only very limited display, 1-10% of the time, will see them last more than a few decades at 50 lux. These occur in all media: oil paint, textiles, tinted paper, coloured inks, and coloured synthetics.
- * Institutions must accept that intermediate colours, although long-lived, are finite. Permanent display at 50-150 lux will cause just noticeable change every few decades, although complete loss will take many centuries.
- * Finally, some good news. Durable to permanent colorants can be illuminated at hundreds of lux for centuries, before showing any change at all. These can be watercolours and gouache just as well as oil and acrylic.

Of course, many institutions don't want to think it through, they want a simple rule. O.K. Light everything organic at 50 lux. If the object is dark or if viewers old, try more, up to 300 lux. The result will be collection roulette: intermediate colours will be well served, fugitive colours will go sooner than most of us want, and durable to permanent colours will suffer low lighting purely for expedience.

I do not wish to suggest that the research has all been done, that it only needs compiling. There is certainly enough to use in the first guidelines from CCI, but there are gaps.

- * What exactly is the rate and effect of light (without UV) on various paper artifacts. Data with UV exposure is much too pessimistic, but by how much.
- * How much do UV filters help specific intermediate and durable colorants. Most industrial data, and too many museological studies, test only with substantial UV present.
- * Do pre-industrial pigments differ much in lightfastness, perhaps due to larger particle size.
- * At what annual exposure do materials durable and permanent to light suffer more from slow thermal and pollution effects than from light. A contemporary oil painting in durable or permanent colours, under UV filtered lights, can be at 300 lux for centuries before fading is even perceptible, let alone substantial. Surely fingerprints, dirt, pollution, accidents and thermal yellowing will take their toll long before light. Such data will help to decide the significance (if any) of very slow light damage.

REFERENCES

1. Thomson, G., "A new look at colour rendering, level of illumination, and protection from ultraviolet radiation in museum lighting", *Studies in Conservation* 6 (1961) 49-70.
2. Thomson, G., "Report by Coordinator", Lighting Group, *ICOM-CC Madrid* (1972) 11/72/4.
3. Thomson, G., *The Museum Environment* 2nd edn. Butterworths, London (1986) p23.
4. Thomson (1986) p23.
5. Macleod, K.J., "Museum Lighting", *Technical Bulletin* 2, Canadian Conservation Institute, Ottawa, (1975).
6. Bromelle, N. "Visual performance with limited illuminance", *ICOM-CC, Madrid* (1972) 11/72/1.
7. Thomson, G. (1986) p.181
8. Ikeda, M., Huang, C.C., Ashizawa, S., "Equivalent lightness of coloured objects at illuminances from the scotopic to the photopic level", *Color research and Application* (1989) 198- .
9. Verriest, G., Buysens, A. and Vanderdonk, R., "Etude quantitative de l'effet qu'exerce sur les resultats de quelques tests de la discrimination chromatique une diminution non selective du niveau d'un eclaireage C", *Revue D'Optique* 428 (1963) 105-119.
10. Crawford, "Just perceptible colour differences in relation to level of illumination", *SIC* 18 (1973) 159-166.
11. Boyce, P., "Visual acuity, colour discrimination and light level", *Lighting in Museums, Galleries and Historic Houses Bristol Seminar*, Museums Association, London (1987) 50-57.
12. Rothko, Mark, letter to Bryan Robertson on how to hang an exhibition at Whitechapel Gallery, cited by M. Compton in the catalogue *Mark Rothko* The Tate Gallery, London (1987) p 59.
13. Loe, D., "Preferred lighting for the display of paintings with conservation in mind", *Lighting in Museums Galleries and Historic Houses Bristol Seminar*, Museums Association, London (1987) 36-49.
14. Stromberg, E., "Dyes and light", *ICOM NEWS* 3 No. 3 (1950).
15. Harrison, L.S., *Report on the Deteriorating Effects of Modern Light Sources* Metropolitan Museum of Art, New York (1953).
16. Judd, *NBS Report # 2254*. I do not have this report, I have used the extensive quotes and references from it contained in Harrison, L.S. (1953).
17. "Preservation of the Declaration of Independence and the Constitution of the United States," *NBS Circular* 505 (1951) See the Appendix.
18. Launer, H.F., and Wilson, W.K. "The photochemistry of cellulose. Effect of water vapor and oxygen in the far and near ultraviolet regions," *J. Amer. Chem. Soc.* 71 (1949) 958-962.

19. Luckiesh, M., *Application of Germicidal, Erythemat and Infrared Energy* Van Nostrand, New York (1946).
20. Taylor, A.H., and Pracejus, W.G., "Fading of colored materials by light and radiant energy", *Illuminating Engineering* 45 (1950) 149-.
21. Morton, T.H., "Practical assessment of the light fastness of dyeings", *JSDC* 65 (1949) 12-.
22. Michalski, S., "Damage to museum objects by visible radiation (light) and ultraviolet radiation (UV)", *Lighting in Museums Galleries and Historic Houses* Bristol Seminar, Museums Association, London (1987) 3-16.
23. Feller, R.L., "The deteriorating effect of light on museum objects", *Museum News Technical Supplement* 3 (1964).
24. Feller, R.L. "Control of deteriorating effects of light upon museum objects", *Museum* 17(2) (1964) 71-98.
25. Feller, R.L. "Studies on the darkening of vermilion by light" *Report and Studies in the History of Art*, National Gallery of Art, Washington (1967) 99-111.
26. Feller, R.L., Curran, M., Bailie, C., *Identification of traditional organic colorants employed in Japanese prints and their rates of fading* Allen Memorial Art Museum, Oberlin College, distributed by Indiana Univ. Press (1984).
27. Padfield, T., Landi, S., "The lightfastness of the natural dyes", *SIC* 11 (1966) 181-196.
28. Thomson, G. (1986) p13
29. Norton, J.E. "A study of the variables encountered in natural light fading", *American Dyestuff Reporter* 46 (1956) 861-883.
30. Cady, W.H., Appel, W.D., *American Dyestuff Reporter* 18 (1929) 407- .
31. Everhard, M.E., Goodhart, F.W., "The fading of F.D.&C red #3 in tablets as a function of concentration, time, and light intensity", *J. Pharm. Sci.* 52 (1963) 281-283.
32. Down, J., "The yellowing of epoxy resin adhesives: report on high intensity light aging", *SIC* 31 (1986) 159-170.
33. Thomson, G. (1986) p183.
34. Rawland, O. "Fading of the British dyed-wool light-fastness standards in the UK, some energy measurements", *JSDC* 79 (1963) 697-701.
35. See the discussion following Rawland (1963) p 714.
36. Michalski, S. "A light damage slide rule: development of the scales", in preparation.
37. Saunders, D., "Colour measurement by digital image processing", *National Gallery Technical Bulletin* 9 (1985) 66-77. This article does not contain the fading data, but it does provide an up-to-date history of the technique, and cites the articles that have emerged.
38. "A light damage slide rule", *CCI Notes* N2/6, Canadian Conservation Institute, Ottawa (1989). \$20
39. Michalski, S., *Light and Conservation Guidelines*, Canadian Conservation Institute, Ottawa, draft (Sept.1989).
40. During UV filtered light ageing at CCI of paint chips from several sample books of the 1920's, the various book and pamphlet papers were not noticeably damaged (in fact they looked better due to some bleaching) despite exposures that badly damaged intermediate colours like vermilion.

ABSTRACT

A wall chart has been developed that outlines preventive conservation, disaster planning, and remedial conservation. It is intended for collection managers, planners, architects, etc. who need an overview of this part of a museum's functions. It is a matrix, with a row for each of nine agents of deterioration. Conservation columns are grouped into building features, hardware features, and procedures. Within each cell of the conservation matrix are five stages 1 avoid sources, 2 detect, 3 block, 4 respond, and 5 recover. These stages uncover a universal pattern in most conservation activity.

KEYWORDS

Theory, planning, preventive conservation, environment

AN OVERALL FRAMEWORK FOR PREVENTIVE CONSERVATION AND REMEDIAL CONSERVATION

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Canada.

Introduction

When I was asked in 1981 to "survey the conditions" in the various buildings of the old National Museum of Man (now the Canadian Museum of Civilization), I discovered that despite museum's preservation function, there was no systematic framework within which to conduct a survey of buildings, let alone an institution as a whole. To make the survey credible, it had to be more than the usual list of grievances. Over the years, the format of that survey developed into a complete wall chart, both for teaching purposes and report writing. It combines elements that traditionally have been fragmented: "museum environment" (light, RH, temperature, pollution), disaster planning (fire, water, physical catastrophe), security, fire prevention, and remedial conservation.

As much as possible, the chart organizes the information by practical categories, not academic disciplines. For example, there is no Department of Biological Control in museums, instead there are resources and authority given to pest control, and others given to humidity control (which controls mould.)

An Overall Framework for Conservation

The chart is a matrix: nine rows for nine agents of deterioration, and columns for implementation. (Fig. 1). The deterioration columns review symptoms for the non-conservator - the engineer, architect, director, or builder - who wonder what the problem is. They also force clarification of the agent of deterioration, e.g. criminals and fire are agents, humidity is not. Incorrect humidity is the agent, and the four types of incorrect humidity cannot be generalized across the collection. They are: 1) very high (mould), 2) fluctuations about some middle value (mechanical damage), 3) above or below some critical RH (mineral specimens, bronze disease), 4) any humidity above 0% (acidic paper, colour photos).

Conservation columns are divided by scale: building, hardware, and procedures. These have obvious bureaucratic and financial significance. Building and hardware usually have separate budgets, consultants, and periods of activity. Procedures really means staff. Someone has to think about something or do something, usually at regular intervals.

Building features and hardware features columns are subdivided into display, storage and transit aspects. Finally, a simple but profound concept I borrowed from the fire prevention theorists: stages. Within each cell of the matrix are five stages: 1 avoid sources of the agent, 2 detect the agent, 3 block the agent, 4 respond to the agent, and 5 recover from the agent. Thus preventive conservation involves the first four stages. Initial recovery from the fast agents (physical catastrophe, fire, water) has traditionally been called disaster planning. Recovery from slow agents (physical neglect, pests, pollution, UV and light, incorrect temperature, incorrect humidity) forms traditional conservation and restoration.

The chart puts the agents of deterioration in rough order of importance. The classic agents of deterioration come first: physical forces, thieves and vandals, fire, water, and pests. The "museum environment" issues come last. In many consultations, the "museum environment" expert or conservator may be the only person representing the safety of the collection. It is crucial that they realize smoke detectors and padded carts are at least as important, though less "scientific" than thermohygrographs (and cheaper). In fact, I now think of the museum environment as all the agents on the chart, not just light and climate.

Paul Marcon at CCI has expanded the building section of the chart on a word processor (Word Perfect) to help write survey reports. It prompts the writer on all the details, and asks for a rating of each - good to non-existent.

Each cell in the matrix is given a two digit number, based on row and column. Eventually, these will correspond to a list of references that provides the reader with greater detail for each topic.

Examples

Consider the agent "Contaminants (air pollution, salts, acids etc.)" Stage 1, avoid sources, at the building stage says: "Air intake avoids local emissions, e.g. roadway; non-emissive building materials." The hardware stage says similar things. The procedures stage says: "Establish a list of noxious building materials and their susceptible artifacts, inform relevant staff. Train staff in the use of gloves." Obviously some contaminants entered the artifact long before the museum collected them. These can only be considered under stage 5, recovery.

Notice that procedures in particular cannot give every detail, but it always refers to specific actions e.g. "establish a list...inform relevant staff...Train...etc." Sometimes, the procedural advice covers a very large action, such as "Establish a fire disaster plan."

Much as museums try to achieve full control at stage 1 (avoid sources) perfection is impossible, so stage 2, detect must always be implemented too. Some of the detection hardware listed in the chart is sophisticated, e.g. thermohygrographs, some is simple, e.g. stick-on shock indicators for crates, paper gas dosimeters anywhere. Under procedures, routine inspection is a major part of detection, as is maintenance and interpretation of detection hardware. The building must be designed to make inspection convenient. And so on.

Stage 3, block, is very practical. It is often more realistic to block pollutants, pests, incorrect humidity, etc. than to avoid them. Then one carries out detection again to check that the block is working.

Conclusions

The chart allows a museum to see at one glance the many facets of conservation, or care of collections, or whatever it's called. Someone or some committee can more readily design good buildings, allocate resources, or simply understand how different museum departments influence conservation. Because the chart is "redundant" museums can often implement control at one scale and not others: with lots of money, the building is the preferred scale, with some money, hardware can work, with no money but people, procedures take precedence.

The chart does not present any new facts. Instead, it uncovers a universal pattern in practical conservation: the five stages. It clarifies agents of deterioration, as compared to vague notions like "temperature" and "relative humidity." At the same time, it is not just a pattern, it contains all the essential details, organized so that an architect can look at one section, a conservator another, and an exhibitions curator another. Each can also see how they fit together, for the good of the collection.

The chart is available in English or French, free of charge from CCI.

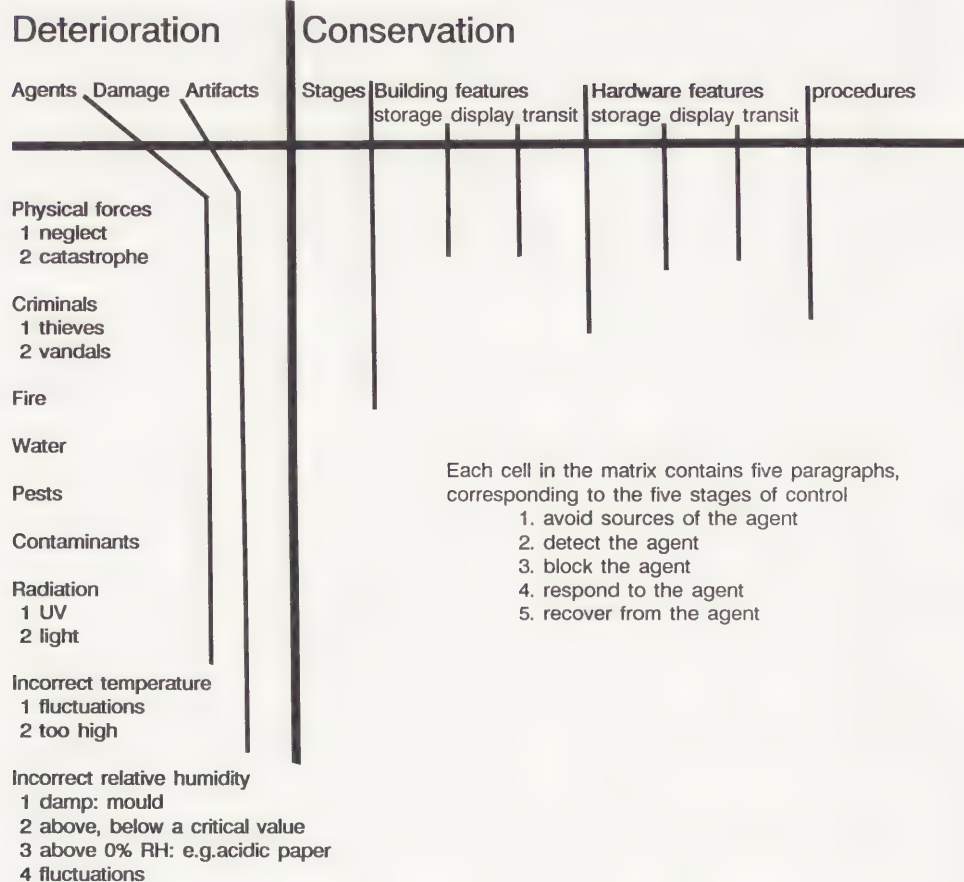


Figure 1 Outline of the headings used in the chart. In full size, the chart is 70cm x 115cm. A reduced version, 31cm x 60cm and still readable, is also available.

ABSTRACT

Temperature and humidity in a large glass showcase for a historical wooden hall were measured and discussed. The conservation facilities including the glass showcase and its shelter were improved according to the proposal of a research committee based on the author's previous investigation. Analysis proved that the improvement succeeded in preventing the penetration of moisture and dewdrops on the glass screen disappeared. But the analysis also proved that the uneven temperature caused by heat entering from the roof produced an unevenness of the RH within the glass showcase. This has brought another problem because it has made it difficult to control RH in the glass showcase at the expected level.

KEYWORDS

temperature, humidity, climate, air-conditioning, insulation

TEMPERATURE AND HUMIDITY IN A LARGE GLASS SHOWCASE FOR A TEMPLE HALL (PART 2)

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1. Introduction

The Konjikido (a small wooden building) was built between 1109 and 1124 by Fujiwara Kiyohira as a mausoleum for himself and as Amida Hall of Chusonji Temple located at Hiraizumi, Iwate prefecture. Konjikido, gorgeously covered in gold leaf, was a symbol of prosperity under the Fujiwaras. At the time of construction Chusonji Temple had about 340 buildings in its compound. But most of them were burnt down or laid waste in the fourteenth century. Fortunately, Konjikido, where the remains of Kiyohira, his son and grandson are still mummified, has survived the centuries.

Konjikido is a single-story, 5.5m long, 5.5m wide and 8.0m high building. It is located in a shelter separated from the visitors' area by large glass screens, thus called "a (large) glass showcase." In 1968, an air-conditioning system was equipped in order to maintain a stable climate in the glass showcase (10-25 °C, 50%RH). In 1986, the Research Committee of the Conservation Facilities of Konjikido, chairman Dr. Masaru Sekino, was organized to improve the conservation facilities.

The author was charged to investigate the climatic condition. The following points were suggested for the improvement of the conservation facilities in a previous report(1):

1. The reason why absolute humidity inside was higher than that outside mainly in spring - a dry season - was that moisture had risen from the ground into the glass showcase (see fig.1). A dehumidifier and a moisture barrier under the floor were necessary.

2. The reason why many dewdrops were observed in early summer on the surface of the glass screen facing outside was assumed to be as follows. Since the temperature change of the ground had a delay of about one month to the outside temperature, the inside air was chilled by the ground in early summer. Then the inside air cooled the glass screen and dewdrops occurred if the surface temperature was lower than the dew-point of the outside air. Heat insulation of the ground and air-conditioning of the shelter were necessary for improvement.

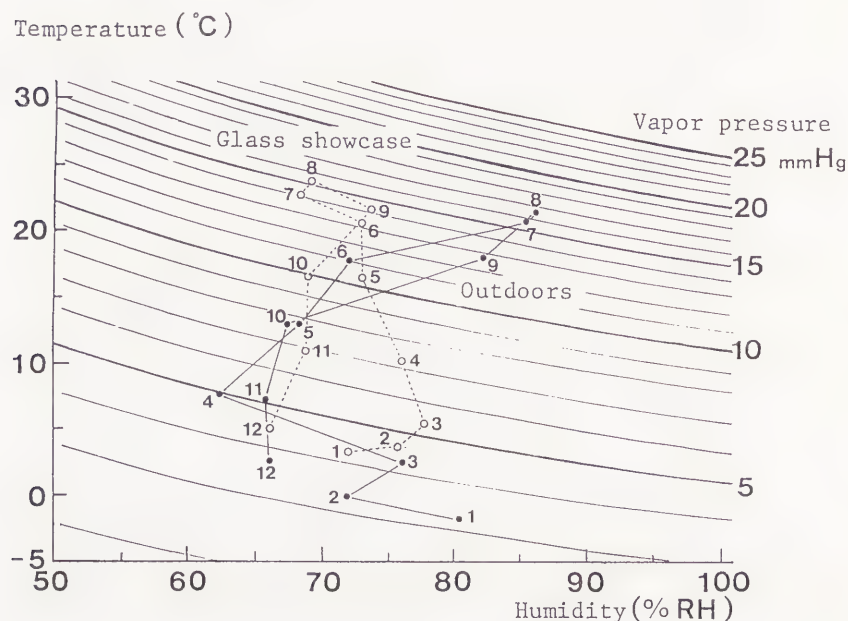


Fig.1 Climate of Konjikido in 1987 (before the improvement).

Considering this previous research, the Committee made a proposal on a plan of improvement for the conservation facilities of Konjikido. The improvement was carried out from December 1986 to March 1990 with financial aid from the Agency for Cultural Affairs. This report describes how the climate within the glass showcase was improved and what problems still remain, which would explain the difficulties of maintaining stable climatic conditions in a very large showcase.

2. Improved Conservation Facilities

The glass showcase has been expanded and totally renewed. Since a quite transparent glass is used for the screen and slightly reddish fluorescent lamps for illumination, the golden Konjikido shines more gorgeously in the new glass showcase.

The new glass showcase has been carefully designed to make it airtight and to keep the relative humidity (RH) inside stable. A moisture barrier and insulation layers have been laid under the gravel on the ground. All gaps in the glass showcase have been sealed thoroughly with silicon rubber. Inorganic moisture buffering material (Muselite(R)) has been used for the back and side walls of the glass showcase so as to prevent a rapid RH change when a dehumidifier works.

Four electric dehumidifiers are used for the improved system in place of the former air-conditioning unit. They have been set in an antechamber which is open to the glass showcase. They are controlled individually; that is, each dehumidifier has its humidity sensor. The four humidity sensors are fixed at the four corners of the veranda of Konjikido, so that the RH can be controlled at 65% even if there is a local difference of RH around Konjikido. Temperature within the showcase is not controlled because daily temperature change is estimated small enough due to air-conditioning of the shelter.

The shelter has been air-conditioned. The entrance of the shelter has also been equipped with an air-curtain, because the door is always opened when Konjikido receives many visitors in a sightseeing season.

3. Measurement

Temperature is measured every minute by Pt resistance thermometers at six points, while humidity is also measured at the same time by electric resistance hygrometers at nine points (see figs.2 and 3). Average values of temperature and RH are calculated every hour and stored in a hard disk of a personal computer (see fig.4). Running times of the four dehumidifiers in an hour are also recorded. Daily reports of temperatures, RHs and running times are printed at midnight.

The collected data are copied to a floppy disk and analyzed at the Tokyo National Research Institute of Cultural Properties.

4. Result

Figure 5 shows the climate of Konjikido in 1989 (after the improvement). Figure 6 shows the average running time of the four dehumidifiers in hours per month. Figure 7 shows the temperature changes at different heights of Konjikido. The apparent difference between the upper part and the lower part of Konjikido was observed from March to September. It is supposed that the heating of the roof of the shelter by sunshine is the reason.

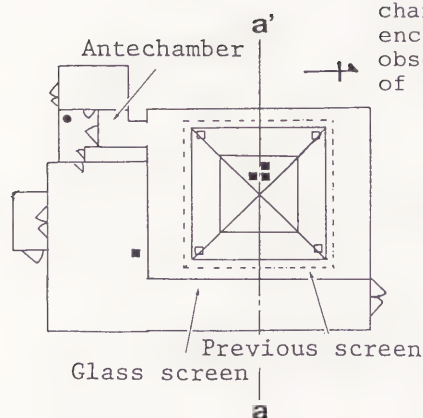


Fig.2 Konjikido, a glass showcase, a shelter and sensors (plan).

- : Temperature & RH sensor.
- : Temperature sensor.
- : RH sensor for a dehumidifier.

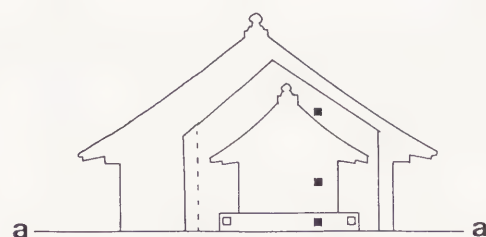


Fig.3 Konjikido, a glass showcase, a shelter and sensors (sectional plan).

5. Discussion



Fig.4 Computer system for measurement and data logging.

Before the improvement of the conservation facilities, the inside of Konjikido was humid (more than 70%RH) even in dry winter conditions and the AH inside was higher than that outside except in rainy summer weather, even though dehumidifiers worked almost all day in the glass showcase (see fig.1). This phenomenon was attributed to rising moisture from the ground as mentioned in the previous report. Figure 5 shows that the AH inside is lower than that outside after the improvement and that the RH inside is kept almost between 60 and 65%. Figure 6 shows that running hours of dehumidifiers decreased even in rainy summer weather. These results indicate that the improved RH condition is realized mainly due to the moisture insulation, even though the four dehumidifiers are set in the antechamber.

Since the temperature inside closely follows the outside temperature and the RH in the shelter is maintained at almost 60% by an air-conditioner, dewdrops on the glass screen have scarcely been observed after the improvement. The air-conditioning of the shelter is also welcomed by the keepers of Konjikido.

In spite of these improvements, the difference of RH within the showcase still brings a problem for conservation. Although the dehumidifiers are set to control the RH inside at a level of 65%, the RH at the middle of the glass showcase decreases below 60%. The committee does not wish the RH to decrease so quickly, because the RH of Konjikido has been kept at more than 70% for a long time and *urushi* (Japanese lacquer) is usually conserved at 65%RH. The setting value of the dehumidifiers can be changed higher so as to keep 65%RH at the middle of the showcase. But this way is not preferable because there is a possibility that the RH under the floor will rise to more than 70% and then mold and insect attacks will occur. It was necessary to find a solution.

Since the AH within the glass showcase is almost uniform, the difference of about 10%RH is probably due to the unevenness of temperature (see figure 7). The best solution is to prevent heat invasion from the roof of the shelter. The committee decided to prolong the work in order to improve the heat insulation of the roof. The work finished at the end of 1989.

6. Conclusion

Due to the improvement of the conservation facilities, rising moisture from the ground and dewdrops on the glass screen have been prevented almost perfectly. But the unevenness of the temperature within the glass showcase has made it difficult to keep the RH at the expected level. This unevenness is thought to be caused by sunshine heating the roof of the shelter. This fact implies that if a careful control of RH is required for a big showcase, thermal insulation and moisture sealing are important in all areas - walls, the floor and the ceiling.

Acknowledgement

The author would like to express his sincere thanks to the administration of Chusonji Temple, the members of the Research Committee of the Conservation Facilities, especially to Dr. Sekino and Prof. Miyano, Mr. Hanzawa and staffs of the Architecture Division of the Agency for Cultural Affairs and his colleague at the Tokyo National Research Institute of Cultural Properties, Mr. Ishikawa. He is also grateful to Mrs. Matsubara and Miss Yagi for their kind help.

Reference

1. S.Miura, "Temperature and Humidity in a Large Glass Showcase for a Temple Hall," *Preprints for the Eighth Triennial Meeting of the ICOM Committee for Conservation* (Volume 3) (Los Angeles: The Getty Conservation Institute, 1987), 897-900.

Materials

1. Trade name: Muselite(R)
Supplier : Asahi Glass Co.Ltd, GRC Division, Muselite Team
Address : 2-1-2 Marunouchi, Chiyoda-ku, Tokyo 100, Japan
Telephone : 03-218-5614

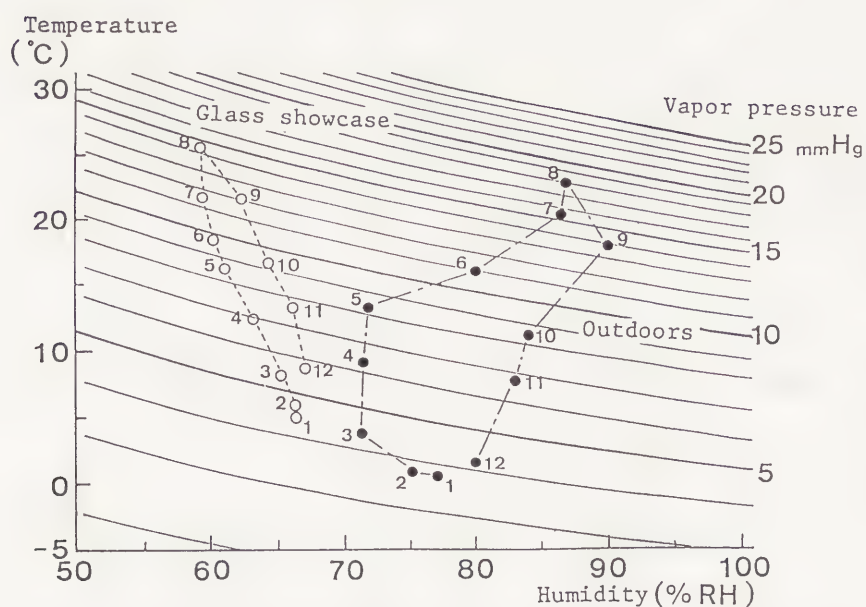


Fig.5 Climate of Konjikido in 1989 (after the improvement).

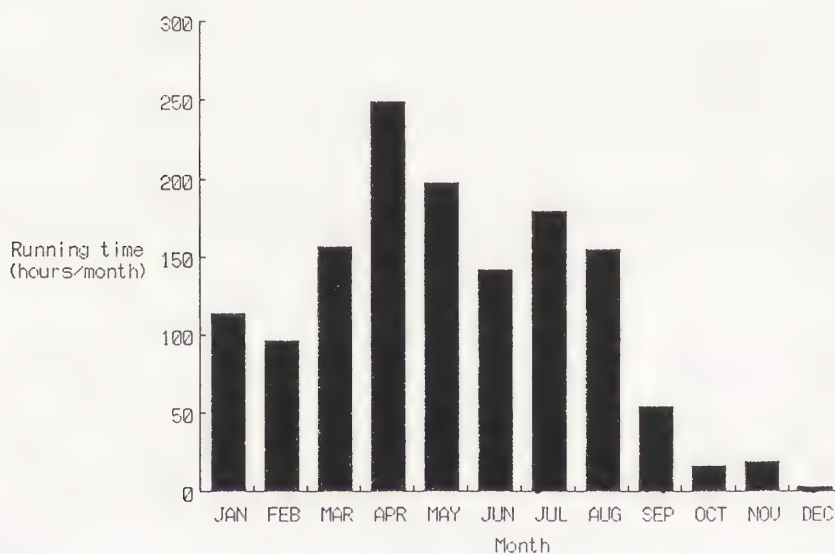


Fig.6 Average running time of the four dehumidifiers in a month.

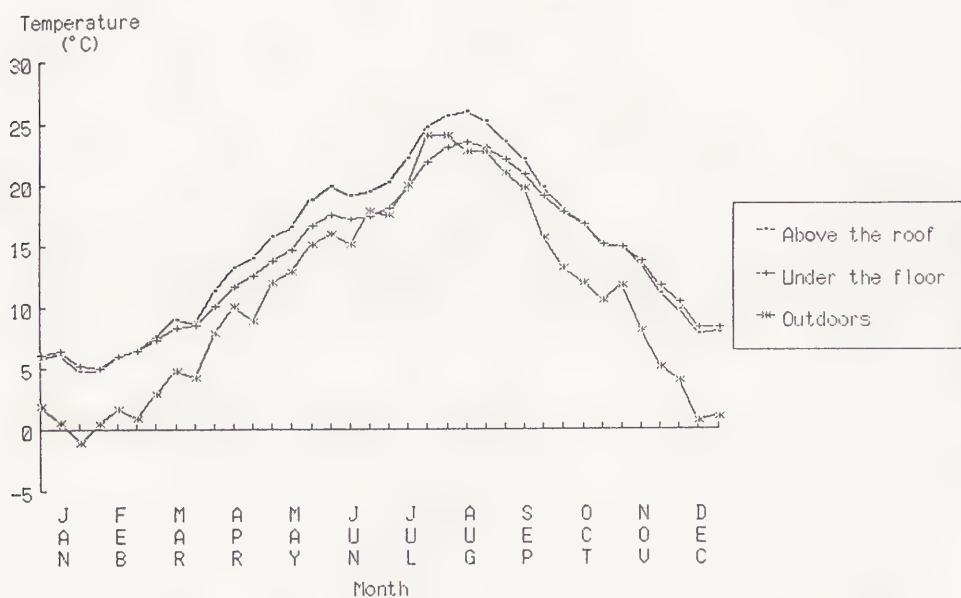


Fig.7 Annual temperature changes of Konjikido in 1989.

ABSTRACT

A computer model of a museum store is used to explore the effects of various methods of air conditioning. A room that is filled with an abundance of hygroscopic material can be held at a constant relative humidity by blowing in a stream of air, about one twentieth of the room volume per hour, which has a water content adjusted to be in equilibrium with the desired water content in the hygroscopic materials. This method works even if the temperature is uncontrolled, because of the buffer effect. The room also needs air recirculation at about one change per hour to ensure temperature uniformity and to allow the removal by filtration of internally generated pollutants.

KEYWORDS

Relative humidity, humidity buffering, air conditioning, climate control.



"The Stradivarius is stabilising the silica gel perfectly, Sir!"

LOW ENERGY CLIMATE CONTROL IN MUSEUM STORES

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Introduction

Orthodox air conditioning consumes a lot of energy. The regulatory system takes air from the room, mixes in a portion of outside air, cools the mixture to the correct dew point and then heats it up again before injecting it into the room. A store room heavily loaded with hygroscopic materials such as wood, paper, and textiles buffers its own climate so well that the continual heating and cooling of the air is unnecessarily fussy and wastes energy.

The concept of relative humidity (RH) buffering by hygroscopic materials in showcases and in packaging for transport is a well understood and abundantly described conservation principle. The same principle applies in storage rooms. The amount of buffer needed is large, if one regards deliberately added buffer as the sole regulatory force. In practice the stored objects and their containers buffer themselves. The distinction between the valuable object and the humble buffer has no meaning in physics. The two materials share the process of moisture exchange which holds them in equilibrium with the surrounding air. Each object surrounded by a mass of its hygroscopic companions fares just as well as one object protected by silica gel.

Experimenting with a whole room is an expensive enterprise so we present here the climate patterns obtained with a computer model made to explore the possible ways of air conditioning the storerooms now being designed for the National Museum of Denmark.

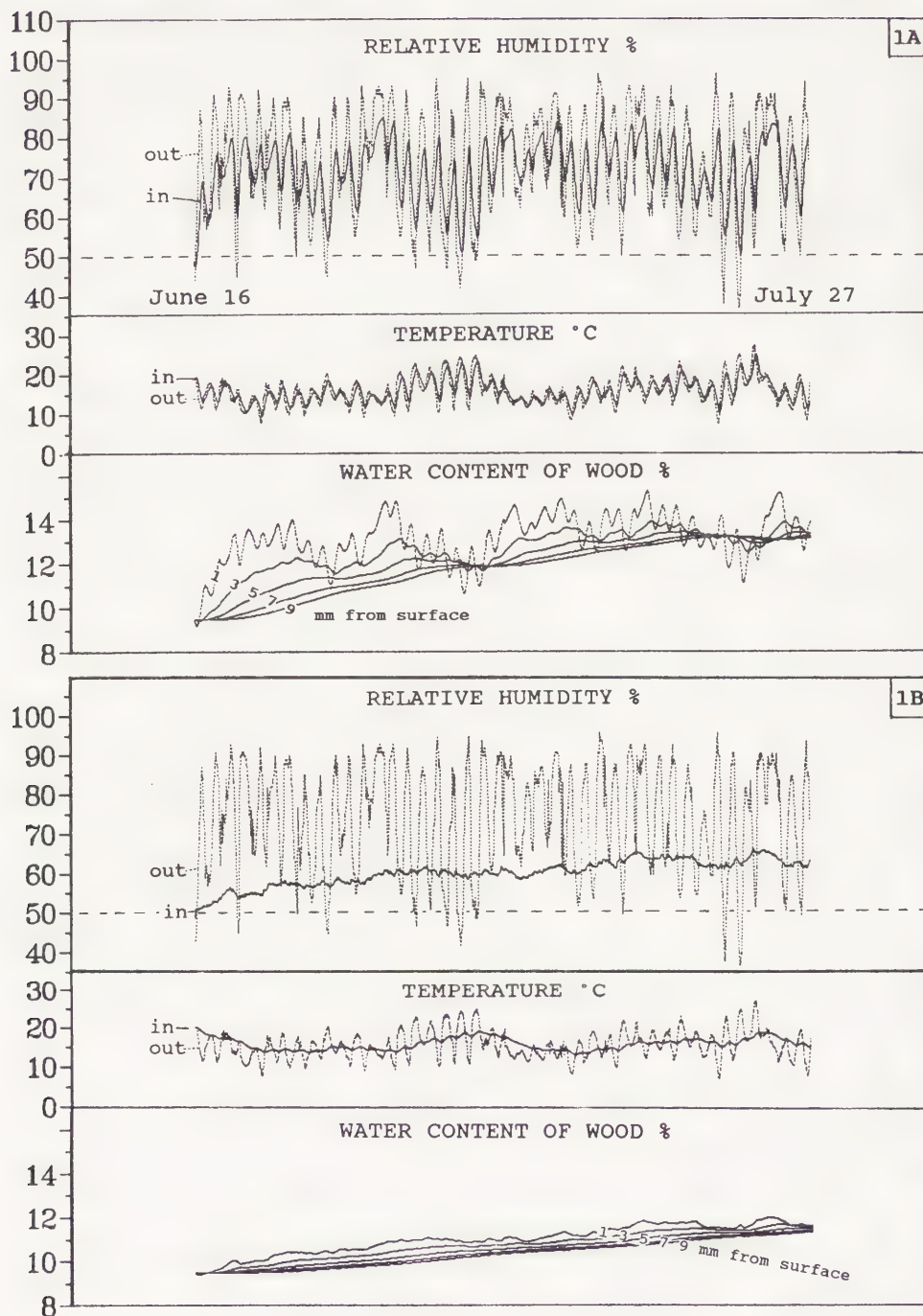
The model

The program calculates the temperature and relative humidity of a room filled with variable amounts of wood, which is our example of a hygroscopic material. The outside climate data are the hourly values of temperature and relative humidity given in the "Test reference year" for Copenhagen (1). The inside climate is calculated every twelve minutes. Heat and water transfers between room air and outside air are calculated using the standard formulae and constants found in air conditioning handbooks (2). The program segment which calculates water vapour exchange with wood uses data from the ASTM standard (3) (see Fig. 2a). This unpublished calculation is described in an appendix. The model is "robust" in the sense that errors in the rate of equilibration of the wood have little effect on the course of the climate. The absorption isotherm of wood is the dominant influence and it is known with sufficient accuracy.

The model room is 15 metres by 30 by 4.5 m high. It has two exterior walls of k value (thermal transmission) $0.2 \text{ W/m}^2 \cdot ^\circ\text{C}$. Ventilation is adjustable from 0.05 to 0.5 air changes per hour. The air is recirculated at one air change per hour. Air speed over the wood surface is 0.1 m/s . A lightly buffered room is represented by 200 square metres of wood, ten millimetres thick, varnished on one side. A heavily buffered room is represented by 5000 square metres of wood. This is not an unusually large amount of hygroscopic material for a store room of this size with a mixed collection. The target RH is set at 50% only to simplify reading the graphs.

On the following pages four control strategies, published (4,5) and unpublished, are interpreted in turn. The computer generated climates are presented in a series of graphs. These show relative humidity and temperature, inside and out, for the period June 16 to July 27 in the "test reference year". Where relevant, the fresh air exchange rate is displayed. For some graphs the moisture content in the wood at various depths is also displayed. There are two sets of graphs for each control method: 'A' shows the climate in a lightly buffered room (200 m^2 wood), 'B' shows the climate in a heavily buffered room (5000 m^2 wood). The graphs labelled 'C' provide data needed to understand the control method, or its effect.

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1. No Control, 0.2 air changes per hour

Without climate control the lightly buffered room 'A' rapidly comes to equilibrium with the outside climate. The buffering effect of the wood surface is rapidly exhausted and diffusion from the deeper layers is too slow to give any help with stabilising the daily fluctuation in RH. The heavily buffered room in 'B' shows the expected slow drift towards the average outside relative humidity. The daily RH cycle is totally buffered, partly by the large area of wood surface but also because of the buffering of the daily temperature cycle by the heat capacity of the wood. The wood moisture content steadily rises towards equilibrium with the outside RH. The winter average relative humidity in Denmark is about eighty five percent so this method of totally passive control will clearly not do. The graph does, however, give some insight into the power of the buffering effect in a well filled room with reasonable ventilation.

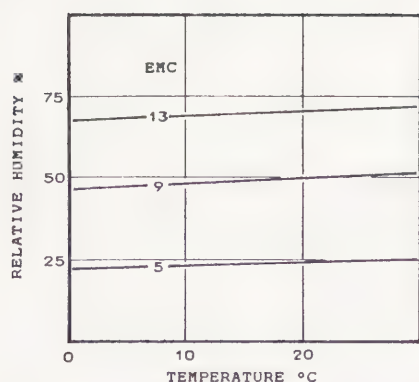
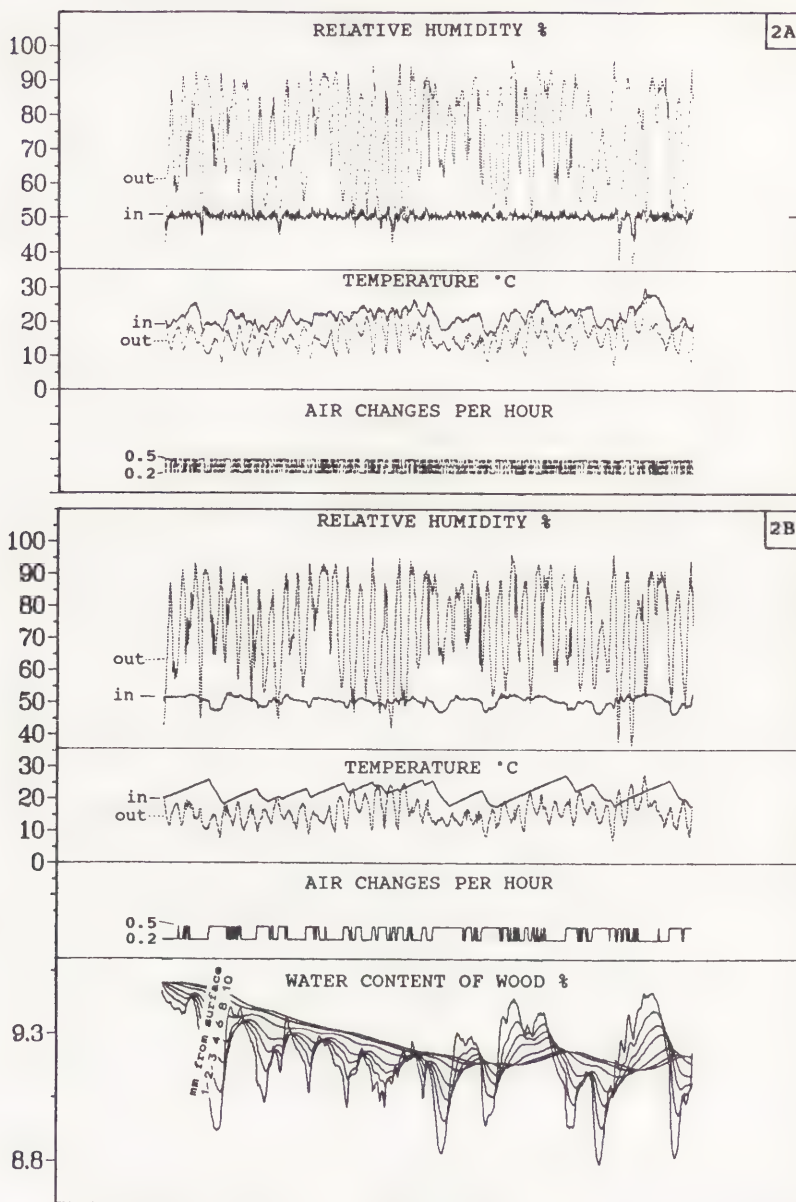


Fig. 2C. Relationship between temperature and relative humidity of air in equilibrium with wood of fixed equilibrium moisture content (EMC). When wood nearly fills a closed container the relative humidity of the air is controlled by the wood, which scarcely changes in moisture content during the process. The relative humidity therefore rises with increasing temperature instead of falling, as it would in an empty container.

Data from ASTM standard
D 2016 - 74 (1983).



2. Relative humidity controlled by raising the room temperature

This method only works where the outside relative humidity is higher than the desired inside RH for most of the time. In our model there is artificial heating but only the natural temperature of the outside air to cool the room. It works well in the lightly buffered room (A). There is considerable waste of energy because periods of heating rapidly alternate with cooling by ventilation.

The method becomes unstable in the heavily loaded room (B). As the temperature rises to try to correct a too high RH the wood desorbs water into the air because its equilibrium water content falls slightly with temperature when the RH is held constant. This small temperature effect becomes significant when the wood to air ratio is large (the process is described in more detail in reference 6). The temperature continues to rise to compensate for the extra moisture from the wood. The room RH does not fall as intended, as the temperature rises. Eventually, at about 30°C, the incoming air, now heated to a very low relative humidity, provides a drying effect too powerful for the wood to compensate. The RH now drops and the control mechanism opens the fresh air vents to cool the room. The cooling wood begins to absorb moisture and the fully open air inlet brings in air of inadequate moisture content to give 50% RH at the high temperature. Both processes further dry the air causing a precipitous fall in RH. The system suffers from a sickness known to engineers as "positive feedback".

Climate control by this means is difficult. At a ratio of about one kg of wood to each cubic metre of air there is no change at all in equilibrium RH with temperature. The correct air temperature must be decided by some other method. An alternative heating control is discussed in the next section.

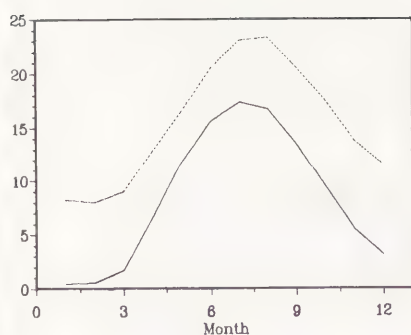
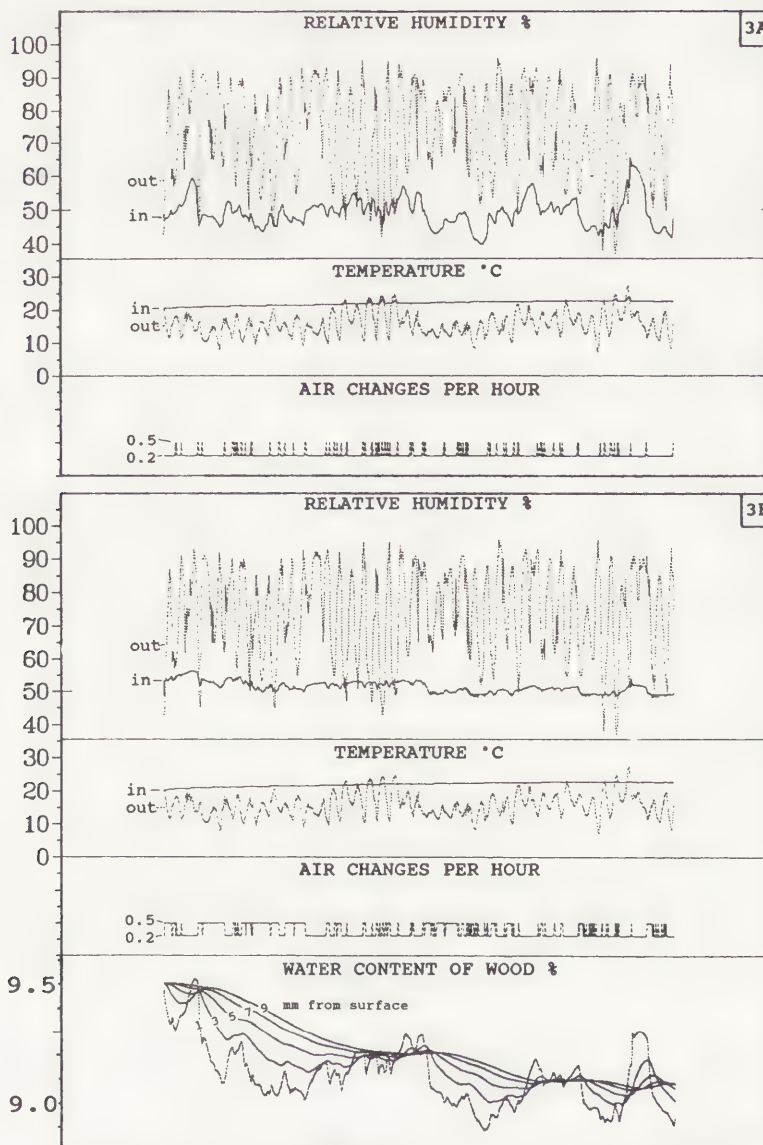


Fig. 3C. The monthly average air temperature in Copenhagen (solid line). The upper, dotted line shows the temperature to which the air must be heated to give it a relative humidity of 50%.



3. Relative humidity controlled by raising the room temperature to the value that would give the correct RH to the average outdoor air for the time of year

This method is similar to method 2 in that heat is used to lower the relative humidity but, instead of reacting to the room climate, the control system imposes a room temperature calculated from the average outdoor climate.

In Denmark in June the average temperature is 15.6°C and the average relative humidity is 68%. If this average air is heated to 20.5°C the relative humidity will fall to 50%. If the room is held at this temperature the probability is that the RH will be 50% indoors. The buffer effect of the wood will hold the air near to this value during periods when the outside air is far from its average value. Furthermore the air exchange is shifted from 0.2 to 0.5 changes per hour when the outside air by chance has moisture content and temperature that would steer the room in the right direction. The monthly average outdoor temperature through the year and the corresponding indoor temperature that gives 50% RH are shown in fig. 3C. In Denmark the relative humidity so rarely falls below 50% that there is no need for artificial cooling. This method is not effective in a lightly loaded room because the length and severity of typical deviations from the monthly average are large enough to overcome the small thermal and moisture buffering effect of the wood. The method becomes more effective as the room fills up. In comparison with method 2 the temperature is of course much more even, the surface moisture content of the wood changes less violently but the internal moisture content is less stable, particularly as the "test reference year" has a cool period in mid summer. A disadvantage of the method is that the temperature is on average some seven degrees above ambient, which accelerates chemical degradation and encourages insect multiplication. Heating is needed throughout the year but energy consumption is smaller than in method 2 because there is no rapid temperature fluctuation.

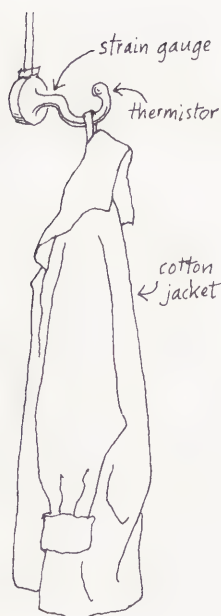
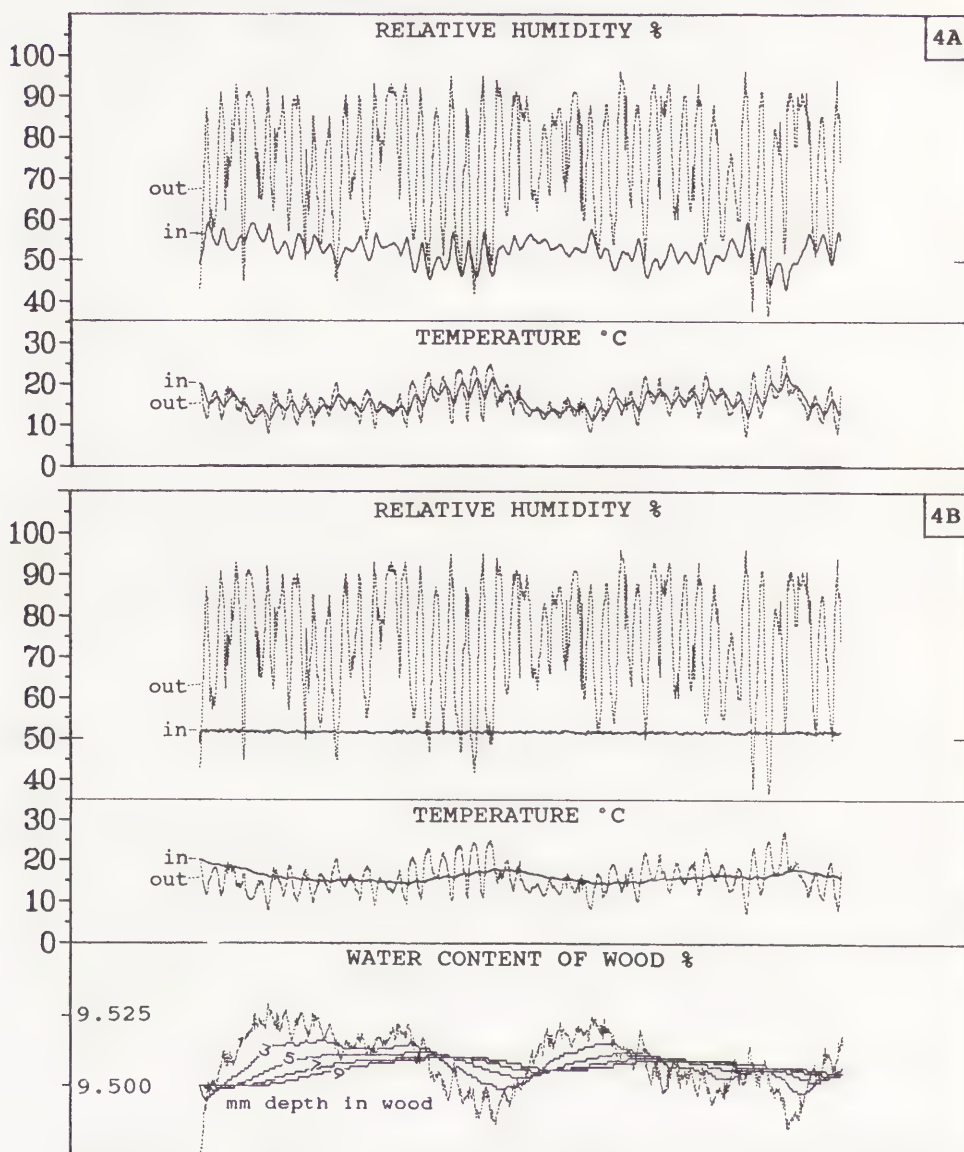


Fig. 4C.

Moisture content sensor.

4. Temperature uncontrolled. A slow air stream is injected at the correct water vapour content to hold a specified moisture content in wood (9.5% for 50% RH).

The purpose of relative humidity control is not really to hold a constant RH but to hold a constant moisture content in hygroscopic materials. A constant RH almost implies a constant moisture content, but not exactly, as Fig. 2C shows. It is more rational to hold the room's contents to a constant moisture content directly, by installing a sensor that measures moisture content directly, by weighing a piece of hygroscopic material. One must also measure the temperature. From these two values the ideal water content of the air can be predicted, and therefore its dewpoint temperature. If a slow stream of outside air is pumped in over a cooling coil at this temperature the room atmosphere will be in perfect equilibrium with the objects. If the room temperature is close to the average outside temperature the necessary dew point will nearly always be below that of the outside air. Humidification will not be necessary. The air flow need only be large enough to compensate for water gain through leakage and diffusion. The heat generated in the refrigeration equipment can be re injected into the air stream. The method uses little energy in comparison with methods that involve heating the air (7).

This method is not particularly effective in the lightly loaded room (A) because the daily temperature change is too fast for effective buffering. In a heavily loaded room (B) the method works perfectly.

Many collections contain objects or packing materials which release corrosive gases. The low temperature will retard the process but it may be necessary to include filters in the recirculation system because the ventilation rate is too slow to flush the room effectively.

Appendix

The calculation of the reaction of wood to changing relative humidity in the surrounding air.

The program is based on an extension of the psychrometric equation to low air speeds and to almost dry materials. The wood is assumed to have a layer of air next to it whose relative humidity is in equilibrium with the moisture content of the wood. The psychrometric wet bulb temperature of this surface layer is assumed to be identical to the wet bulb temperature of the room air outside the boundary layer. If room air and wood are not at equilibrium the boundary layer will have a different RH from the room air but will nevertheless have the same wet bulb temperature. The surface temperature of the wood can therefore be calculated by working the psychrometric equation backwards. The temperature difference between wood surface and room air causes a heat flow which can be calculated from standard formulae for the heat transfer coefficient. This heat vapourises water from wood. The heat of desorption of water from wood is a function of temperature and of water content.

In this way the water movement through the wood surface can be calculated. The further movement of water through the wood is calculated by applying Fick's law of diffusion between a series of thin layers, each of which is assumed to be of uniform water content. The diffusion constant of water through wood is also a function of temperature and water content.

Conclusions

There are important differences in the climatic needs of storage rooms and of exhibition or office rooms: in the store the temperature can be much lower and can be allowed to fluctuate, slowly, over a considerable range. Most museum objects benefit from, or at least tolerate, a lower temperature than humans. The ventilation rate can be low because people only occasionally visit the store room. These differences are exploited by method 4. The method is, however, flexible enough that it will also work in heated rooms. If the indoor temperature is below the dotted line in fig. 3c the ideal dewpoint inside is below the outside value for at least half the time and the system will function well. If the room temperature rises still higher it will be necessary to humidify the airstream. This is quite easy to do if the exchange rate is kept low, but the economic advantages diminish.

Our conclusion is that the best low energy method for climate control in store rooms in a temperate climate is to pump into the room an air stream, calculated to be just sufficient to compensate for natural leakage, which passes over a cooling coil whose temperature is controlled by weight changes in a piece of wood, or cotton (or an equivalent value calculated electronically from RH and temperature measurements), so that weight gain causes a lowering of the cooling coil temperature, and thus a lowering of the dew point of the air, and vice versa. A separate air recirculation system holds a uniform (but not constant) temperature throughout the room. It may be necessary to install air filters to absorb pollutants that are not sufficiently diluted by the slow stream of fresh air. The room should be well insulated and sealed against air flow through the walls and around doors and windows. Construction materials should not outgas pollutants. The running cost of this system will be low and the environmental quality will be high.

The quick reaction of orthodox air conditioning systems is unnecessary and wasteful when used to control the sluggishly reacting mass of objects in a museum store. A gentle push towards the right moisture content is all that is needed.

Acknowledgements

We thank P. Kjærulf-Jensen for fruitful discussions.

Notes

1. Test reference years are available for much of Europe. They are published by the Commission of the European Communities. Tape or disc can be obtained from the various national meteorological institutions or from: Cenergia ApS, Walgerholm 17, DK-2750 Ballerup, Denmark.

2. The most accessible standard reference work is the Handbook of Fundamentals (metric edition), published by the American Society of Heating, Refrigeration and Air conditioning Engineers (ASHRAE).

3. American Society for Testing and Materials (ASTM) Standard test methods for moisture content of wood D 2016-74 (1983).

4. Sarah Staniforth and Bob Hayes, "Temperature and relative humidity measurement and control in National Trust houses," Preprints of the 8th meeting of the ICOM Committee for Conservation, Sydney (1987), 915 - 926.

5. Raymond H. Lafontaine and Stefan Michalski, "The control of relative humidity - recent developments," Preprints of the 7th meeting of the ICOM Committee for Conservation, Copenhagen 1984, pp 84.17.33 - 37.

6. Tim Padfield, Martin Burke and David Erhardt, "A cooled display case for George Washington's Commission," Ibid. 84.17.38-42.

7. Sarah Staniforth and Bob Hayes, "Keep the Old Piles standing," New Scientist No 1678, (19 August 1989) 37 - 41.

ABSTRACT

THE LOGGING OF LIGHT LEVELS IN NATIONAL TRUST HOUSES

A portable battery-operated data logger for light levels is described. Recordings can be used to estimate equivalent annual light exposures and light distribution within rooms. Exposures of oil paintings at Clandon Park are found to be well within the recommended maximum, and the exposures of the most light sensitive materials are at approximately the recommended level. Manually operated sun blinds, the traditional method of light control practised in historic houses in England, are found to give preferred viewing conditions for oil paintings as indicated by recent research.

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Introduction

Since 1985, the National Trust has been using battery-operated solid state memory data loggers to record temperature and relative humidity levels (1). These have proved very appropriate in historic houses. They can be moved from room to room within a house as they do not require permanent installation of wiring, which would be intrusive to the fabric of the buildings. 50 of the 120 houses with collections of artefacts are now monitored in this way. The recordings have been invaluable in enabling recommendations to be made for the improvement of environmental conditions, and checking that control methods are effective.

The monitoring of light levels has been far more laborious (2). Each house has a hand-held light meter which is used for taking spot readings. We have not established a routine for doing this, because light levels are so dependent on weather, date and time. We have suggested that house staff should experiment by taking readings at many points in a room to get an idea of light distribution. Obviously the enthusiasm with which they do this, and the use that they make of the information is entirely dependent on the member of staff involved. None of the house staff are professional conservators, and although training courses include instruction on light and environmental control, we cannot hope that they will devote the time and energy to this particular task that might be expected of a member of the conservation staff working for a museum.

KEYWORDS

Data logger, light, light
exposure, historic house

Only one or two houses have rooms with automatically-controlled blinds installed. Almost all have cream or dark-coloured cotton roller blinds or curtains which are opened or closed manually according to the amount of daylight available. If the sun can shine directly into a room then the blinds are closed. On a gloomy day, the blinds are fully opened. On most days on which houses are open during the summer season (April to October), the light will change during the day, and the height of blinds has to be adjusted accordingly. House staff are instructed to set the level of the blinds using a hand-held light meter. Our specification is to reduce the light levels to 50 lux on any light-sensitive object. Almost all rooms contain organic materials that fall within the most light sensitive category, and therefore it is not possible to distinguish between 200 lux and 50 lux specifications. We do not have a sufficiently sophisticated method of control that would allow oil paintings to be lit at 200 lux while the 18th century silk on which they hang is only exposed to 50 lux!

The problem is knowing where to take a light reading in a room, that is representative of the light levels throughout the room. We need to know if light distribution within a room remains constant as the sun moves round a house, or if it is dependent on the position of the sun in the sky. If the light distribution is constant, then house staff can be instructed to take light readings in one place in a room, and set the blinds to get a certain level there, and know that no sensitive object in the room is exposed to more than 50 lux. As almost all rooms are lit from side windows, then light distribution is likely to be more complex than in a sky-lit museum room. It is unrealistic to expect to be able to carry out a survey like this using manual readings, and therefore we needed an automatic method of monitoring light levels.

Instrumentation

An instrument was needed that could be moved from room to room and be set up on a temporary basis. The obvious data logger to use was the 'Squirrel' manufactured by Grant Instruments (3) that was already being used extensively for environmental monitoring. The National Gallery had a similar application and had already used a Squirrel meter/logger with Megatron photocells and amplifier (4).

An 8-bit Squirrel meter/logger with a 64,000 readings capacity memory was bought. It has 16 input channels, of which 14 respond to input voltages between 0 and 5 volts. 12 of these are to be used with photocells, and the other 2 with temperature sensors. The last 2 channels take input from relative humidity sensors, which means that temperature and relative humidity can be recorded in 2 locations, as well as light levels from 12 positions.

12 Megatron photocells are used (5), 2 for exterior use and 10 for interior. Megatron Type M 25 mm cosine-corrected photocells in weatherproof mounts are used for exterior use. They are fitted with 20 metres of cable. Megatron Type M 16 mm cosine-corrected photocells in plastic mounts are used for interior use and are fitted with 10 metres of cable.

The signal produced by the photocells is too weak to be measured directly by the Squirrel, and has to be amplified. The 12 sensors are connected to 12 amplifier circuits (5) which are individually calibrated to give an output voltage proportional to the light incident on the photocells. The calibration of the photocells is given in Table 1. For example, photocell 7, which is calibrated to give a full scale reading of 500 lux, will register 1 volt on the Squirrel when 100 lux falls on the photocell. As an 8-bit Squirrel is used, the voltage registered is digitised to 250 levels, therefore the lux levels will also be calculated at 250 levels. Photocell 7, will have a minimum lux step of 2 lux. These minimum steps are also shown in Table 1.

Table 1

Calibration of photocells

Photocell number	5 volts given by (lux)	Minimum step (lux)
1 - 2	50,000	200
3 - 4	5,000	20
5 - 6	2,500	10
7 - 10	500	2
11 - 12	250	1

The amplifier is battery operated by six 1.5 volt size C batteries. Megatron say that these should give 35-70 hours of continuous use. This would not be anything like comparable with the battery life of the Squirrel (up to six months) if the amplifier were left switched on all of the time. However, the Squirrel has a very useful function which allows it to output signals before and after making measurements. This facility is used to switch the amplifier on and off. Each time the amplifier switches on automatically it will be for less than 10 seconds, and therefore the battery will easily last for the time that it takes to fill the memory of the Squirrel. For example, if the Squirrel is used just for light readings from the 12 photocells, it will take 5,333 sets of readings to fill the 64,000 reading memory. The amplifier will be switched on for less than 53,330 seconds, or 15 hours. Much less than the battery life claimed by Megatron.

Photocells have been attached to the outside walls of the house by tying to nails driven into mortar. On the inside, 'Blutak', a plastic dough, has been stuck onto modern areas of paintwork. The smaller photocells are very light, and the 'Blutak' has proved a quite satisfactory method for holding the photocells in place.

The Squirrel has been set to record every 15 minutes. With 12 photocells attached, the memory will be filled in just under 56 days. In practice, the readings have been extracted from the Squirrel approximately once a month. The longest recording interval was six weeks. The data from the Squirrel is extracted using software provided by Grant Instruments. A portable computer, Sharp PC-4641 with 40 MB hard disk, is taken to the house. It is IBM-compatible, and the data is transferred into an IBM-compatible PC in the office.

Light recordings at Clandon Park

Clandon Park is an 18th century house designed by a Venetian architect, Giacomo Leoni. It is approximately 50 kilometres from London. It proved to be a good house in which to assess the usefulness of the first of these light level loggers for the National Trust. It has showrooms orientated towards all points of the compass. The instrument was first installed in May 1989, and was used to record light levels in three rooms during the open season until the middle of October 1989. The summer of 1989 has been one of the sunniest in England this century, so the results have given us a good indication of the effectiveness of the cream-coloured sun-blinds installed at the house.

The Morning Room is on the south-west corner of the house. It has one large window facing south and two large windows facing west. One of the photocells for exterior use was positioned on the south-facing outside wall and the other was positioned on the west-facing wall. 9 of the photocells for interior use were positioned around the room, adjacent to light-sensitive materials. One photocell (Channel 12) was not used.

In this room, the most important contents are oil paintings and ceramics. There is an early 18th century needlework carpet on the floor in front of the chimneypiece.

The position of the photocells and the average illuminances that they recorded during three recording periods in May and June 1989 are given in Table 2. The 'crudeness' of the averages is a consequence of using an 8-bit Squirrel.

The average lux levels are a measure of the average hourly exposure for the given recording period. During each recording period the house is closed at night time and for two days per week, and the computer programme averages these times of zero illuminance along with the recorded light levels when the house is open. By multiplying the average illuminances by 24, we arrive at a daily exposure. During the winter, the house is closed, and the rooms are exposed to zero illuminance. By multiplying the daily exposure by the number of days of the open season, a very crude assessment of the annual exposure can be made. During 1989, the open season for Clandon Park was 210 days. A multiplying factor of 5000 (approx 24 x 210) has been used to arrive at an approximate equivalent annual exposure for each recording point. These values are also given in Table 2.

Table 2

Position of photocells, average illuminances and approximate equivalent annual exposures in the Morning Room, Clandon Park

Photocell Number	Position	Average illuminance (lux)	Approximate equivalent annual exposure (lux hours)
1	Outside, facing south	10,200	-
2	Outside, facing west	9,000	-
3	Inside, facing west	40	200,000
4	Inside, facing south	20	100,000
5	Inside, facing west	50	250,000
6	Inside, facing east	20	100,000
7	Inside, facing east	18	90,000
8	Inside, facing east	30	150,000
9	Inside, facing north	30	150,000
10	Inside, facing north	30	150,000
11	Inside, on carpet	33	165,000

These annual equivalent exposures are well within the figure of 650,000 lux hours, the figure quoted by Garry Thomson (6) as the recommended annual exposure for paintings exhibited at 200 lux. Photocell 11, which was placed on the needlework carpet, is exposed to about the recommended maximum exposure for 50 lux materials.

Graphs of light levels can be printed out. The computer programme allows selection of the time period and expansion of the data axis. It also allows up to four channels of data to be printed on the same graph. This allows great versatility for examination of the data. In fact, almost the greatest problem with this study has been making sense of the large amount of data. It has been difficult to present the data in a way that can be readily understood and used, both for circulation among National Trust staff and for this paper!

A small selection of graphical print-outs are shown in Figures 1-4.

Figure 1 shows the print-out for photocell number 3. This photocell was inside on a west-facing wall. The data axis has been expanded to print-out from 0-500 lux. This channel is calibrated from 0-5000 lux, but the maximum level never rose above 500 lux. The data is printed out for the whole of the 16 day recording period. The house is closed on Thursdays and Fridays. The graph shows very clearly that the room was kept dark on both of these closed days. However, on this time scale it is difficult to see details about the light levels, and it has been more informative to print out a recording of one day, to demonstrate a number of interesting features. The rest of the graphs show the light levels recorded on Saturday 27 May 1989.

Figure 2 shows the light levels recorded by the outside photocells. The sun moves round the house, so the maximum level is recorded by the south-facing photocell in the morning, and by the west-facing photocell in the later afternoon. In fact, the light readings go above the range of the photocell between 15.30 and 17.30, that is above 50,000 lux. The Squirrel registers the scale maximum for this time. It can also be seen that sunrise was at 05.00 and sunset was at 21.00.

In Figure 3, the light level recorded by the outside photocell pointing west is compared with one of the inside photocells that also points west. One of the features of this graph is the clear demonstration of the time at which the staff have opened and closed the shutters. The shutters are opened on open days at 08.30 and closed shortly after the house closes at 17.00. One of the most pleasing aspects of this summer's recording at Clandon Park is the house staff's strict observance of the elimination of all light when the house is closed. During the morning, while the room is cleaned, the cream-coloured blinds are left fully closed. The south-facing blind is then opened partially, or fully at just before 13.30 when the house opens to the public. This allows visitors a view of the garden, preventing a claustrophobic feeling while in the house. By this time, the sun has moved round and no longer shines directly into the room. The amount that the south-facing blind is opened depends on the weather, and the light levels measured in the room. One of the weaknesses of this study is that no record of when blinds were opened or closed was made. Higher light levels are consistently recorded during the afternoons, when the house is open.

Figure 4 shows the readings recorded from photocells pointing west (Channel 3), east (Channel 7) and north (Channel 10). It is interesting to note how similar the variation in light levels is, albeit at different levels. There is more or less a constant ratio between the three channels. This remains true whatever combination of channels is selected; these three were selected as the readings are well spread out on the graphs. This is the result of the highly diffuse nature of the daylight entering through the cream-coloured blinds, which eliminates the directional quality of the light. This fact is encouraging, and suggests that it is possible to take a light reading in one position of the Morning Room, and know that this can be simply related to other positions in the room by a multiplying factor.

Recording of light levels in the Speaker's Parlour, which has windows pointing west and north, and the Hunting Room, which has windows pointing east and south, were made from July to October. Data could be presented in a similar way to that recorded in the Morning Room, but lack of space precludes its publication here. In summary, average illuminances were calculated, which were similar to those in the Morning Room, and showed that light distributions around the rooms were related to each other by a simple multiplication factor.

Conclusion and further work

There are two obvious ways in which these light levels can be used: to provide an estimate of the annual equivalent exposure, and to give multiplication factors relating light distribution around rooms. Once the way in which the light distribution varies around a room has been determined, a representative point can be selected at which the house staff can take a manual light reading when they are adjusting the blind level.

It is quite clear from the recordings taken during this summer in the Morning Room at Clandon that the light levels rise considerably above the 50 lux specification. The maximum level recorded at any point in the room was 640 lux. In fact, with the exception of the needlework carpet on the floor, all the light sensitive contents of the room are oil paintings, which fall into the 200 lux category. The approximate equivalent annual exposures calculated from the average illuminances are well within the value recommended by Garry

Thomson (6). The light level fluctuates with the daylight levels entering through the windows, and when the blinds are drawn, through their fabric.

These fluctuating daylight levels, with views to the outside through some of the side windows, are the conditions found to be preferred for the viewing of oil paintings, in research carried out by David Loe (7)! It is amusing to discover that traditional housekeeping practices, applied in houses in England since the 17th century, manage to produce the conditions that not only conserve their contents, but also provide good viewing conditions for the appreciation of paintings! As we have also found with relative humidity levels in National Trust houses (1), conservation science is now recommending environmental conditions that were achieved by tradition and practice in historic houses.

It would be interesting to compare the estimates of annual equivalent light exposures with the fading shown by blue wool standards. We have begun to use these in National Trust houses, as they give a graphic demonstration of the damaging effect of light to sceptics. During the summer of 1990, when light recordings will be made in another National Trust house, blue wool standards will be placed alongside photocells and will be left for the whole open season, even when the data logger is moved to a different room.

It is clear from the light levels recorded at Clandon, which is one of the lightest National Trust houses, that it was unduly pessimistic to have two photocells calibrated to read up to 5000 lux, and another two calibrated up to 2500 lux. During the winter of 1989-90, these photocells will be recalibrated by Megatron to read in the range of 0-500 lux. This will be done as part of the annual recalibration and service of the equipment.

One issue that is becoming a general problem for those of us involved in environmental monitoring projects is the vast amount of data generated. There is a danger in drowning in the number of numbers! It is pointless to generate more information than can be reasonably acted upon, and therefore the National Trust does not intend to purchase any more of these light level dataloggers until it has the staff to service them. This argument is equally applicable to temperature and relative humidity monitoring, and a discussion among those members of the Climate and Lighting Working Group who are involved in data logging, about ways of summarising and presenting environmental data, would be of great value.

Notes and references

1. Staniforth, S. and Hayes, B., 'Temperature and relative humidity measurement and control in National Trust houses', in Preprints of the 8th triennial meeting of the ICOM Committee for Conservation, Sydney, 1987. Vol III 915-926.
2. Staniforth, S., 'Light and environmental control in National Trust houses', in Recent advances in the conservation and analysis of artefacts, Summer Schools Press (1987) 327-334.
3. Squirrel meter/logger SQ64 14U/2L, IBM PC analysis program from Grant Instruments (Cambridge) Ltd., Barrington, Cambridge CB2 5QZ. Telephone 0763 60811. Cost approximately £1000 for meter/logger.
4. Saunders, D., 'A portable instrument for the logging of light levels' The Conservator 13 (1989) 25-30.
5. 12-channel amplifier and photocells from Megatron Ltd., 165 Marlborough Road, London N19 4NE. Telephone 01 272 3739. Cost approximately £1500.
6. Thomson, G., 'The Museum Environment', (London, Butterworths, 2nd edition 1986) p 30.
7. Loe, D.L., Rowlands, E. and Watson, N.F., 'Preferred lighting conditions for the display of oil and watercolour paintings' Lighting Research and Technology 14 (1982) 173.

Acknowledgements

The National Trust is grateful to the Conservation Unit of the Museums and Galleries Commission for an Equipment Grant that contributed towards the purchase of the data logger.

Figure 1

Light levels in Morning Room, Clandon Park. 22 May - 7 June 1989

Channel 3 - inside facing west

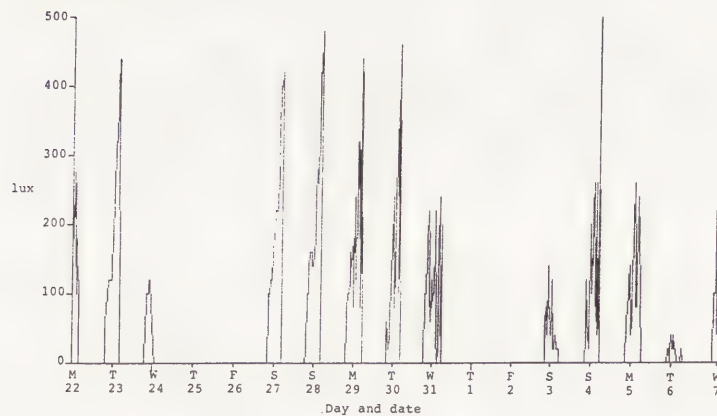


Figure 2

Light levels outside Clandon Park. 27 May 1989

Channel 1 - outside facing south

Channel 2 - outside facing west

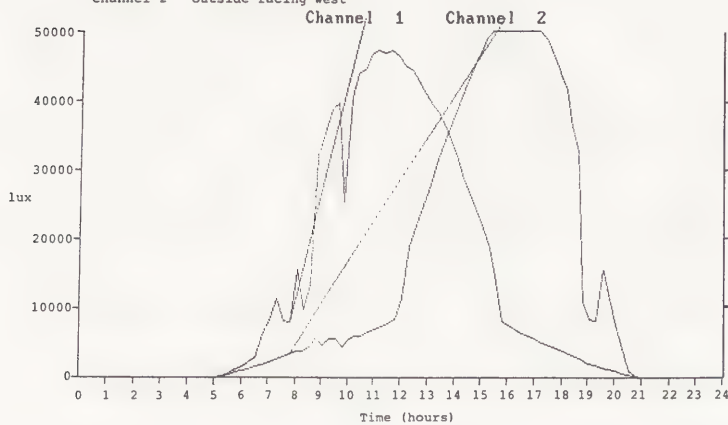


Figure 3

Light levels in Morning Room and outside Clandon Park. 27 May 1989

Channel 2 - outside facing west

Channel 3 - inside facing west

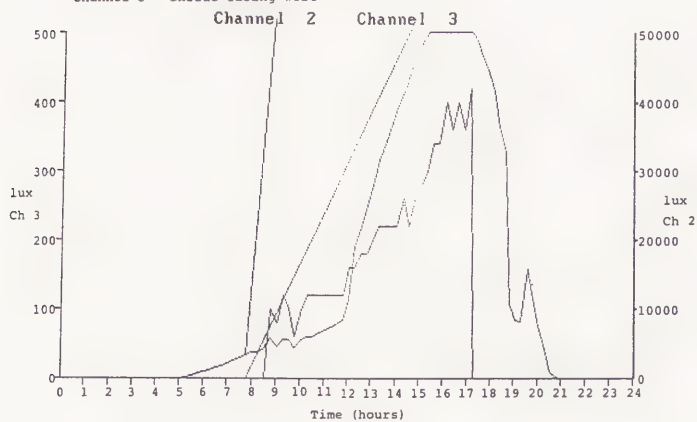
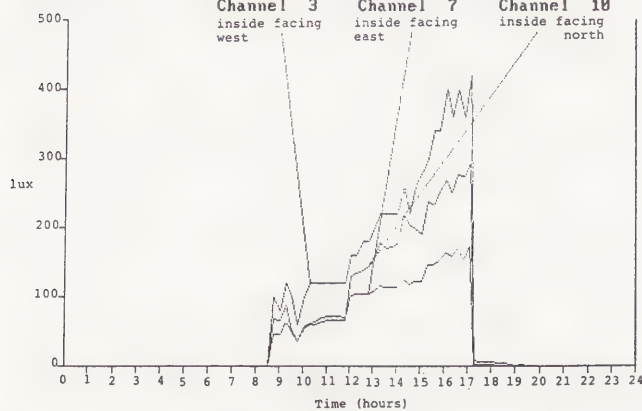


Figure 4

Light levels in Morning Room, Clandon Park. 27 May 1989

Channel 3
inside facing
westChannel 7
inside facing
eastChannel 10
inside facing
north



Working Group 18

Conservation of Leathercraft and Related
Objects

Conservation des cuirs artisanaux et objets
similaires



ABSTRACT

The wall hanging and its state of conservation are described: still in the place for which it was conceived, the hanging is complete and in reasonable condition.

Given the lack of information on flock leather, references were collected on the history and technique of this unusual type of artifact, of which only some rare examples remain. Archival documents were also found, which permitted the dating of the installation of the hanging. The results of the first investigations on the constituent materials are given.

KEYWORDS

Flock-leather - gilt leather - Roman Baroque leather wall-hangings - analysis of tannins.

THE SEVENTEENTH-CENTURY FLOCK-LEATHER WALL HANGINGS OF THE CHIGI CHAPEL IN ARICCIA: A CASE STUDY

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The hangings sumptuously adorn the private chapel of the Chigi Palace at Ariccia, 27 km from Rome. The building was constructed by the Savelli family in the second half of the sixteenth century, and passed into Chigi hands in 1661, together with the entire fief. This was the family of Pope Alexander VII (1655-67), and his nephew, Prince Agostino, used the palace as his country home (1). After having the village radically rebuilt by Gian Lorenzo Bernini, in the period from 1666 to 1671 the Chigi also promoted a major expansion of the building itself. Upon completion of the works, in November 1672 the architect Carlo Fontana conceived an elaborate stage set for a musical performance in the *Sala Maestra*. At that time, the palace, almost completely rebuilt, was already lavishly decorated. According to an inventory dated 18 May 1672, there were leather wall hangings in a good 24 rooms; in 7 of the rooms, new hangings had been installed between February and April of that year (2). The wood blocks for these were commissioned in August 1671 from Paolo Franceschi (3). The chapel, which leads off the *Sala Maestra*, is situated in the oldest wing of the building. It was probably embellished with flock-leather for the festivities in 1672. The wall decoration, not mentioned in the inventory of May 1672, is minutely described in that of 10 January 1673, where it is said to have been "brought from Rome" (4). Several examples of the rich leather wall hangings — gilt, painted, embossed and flocked — still survive today (fig. 1).

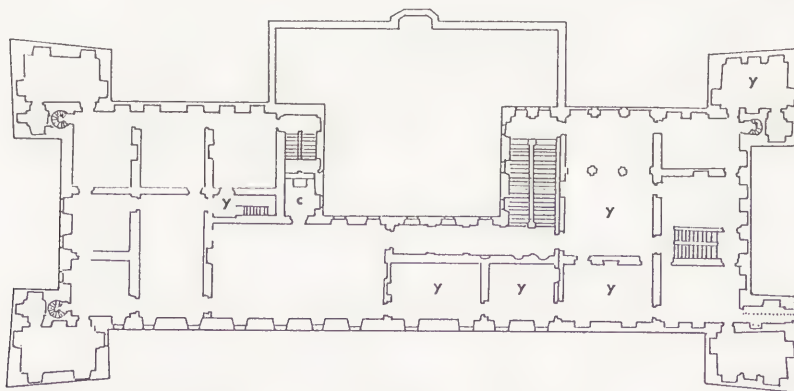


Fig.1) Plan of *piano nobile* (from a drawing by Carlo Fontana ca. 1666).
Rooms with leather wall-hangings are marked with a 'Y', the Chapel is marked with a 'C'.

The palace was ceded by the Chigi to the town of Ariccia in December 1988, and will be restored for public use. In view of the restoration and the future destination of the building, the Italian Central Restoration Institute, in collaboration with the National Agency for Research in Nuclear and Alternative Energy (ENEA) and the Superintendence for the Artistic and Historic Heritage of Rome and Lazio, has begun a series of physico-chemical surveys in order to determine the best conditions for conservation of the furnishings. At the same time, study of the leather hangings was initiated, focusing on their state of conservation and precautions to be taken during the restoration of the building. Research in the Chigi archives was also undertaken.

Given the unique character of the hangings adorning the chapel, it seemed of interest to mention the work at this conference, and also to provide some information on the early results of the various aspects — historical, technical and scientific — of the research that is going forward.

1. "Flocking" — Historical and Technical Notes

Flocking, or fiber powder obtained when cloth is shorn, is applied specifically in the arts and crafts for the imitation of fine and costly fabrics; dyed in various colors and applied with an adhesive on different supports, such as linen, cotton, silk, leather, paper, etc., flocking can simulate the fine weaving of figured or brocaded velvets, damask and tapestries. There are references to the use of this technique, which is quick and easy to use, as early as the last quarter of the fifteenth century (5), but it is not until the seventeenth century that information on materials and techniques is found.

Indeed, the two principal documents on flock-leather date to this century. The first is a patent granted in 1634 by Charles I of England (6). The text, first cited by Beckmann (7), acknowledges Jerome Lanier's invention of a special technique, which functioned "by affixing of wool, silk, and other materials of divers colours upon linen cloth, silk, cotton, leather and other substances, with oil, size and other cements, to make them usefull and serviceable for hangings and other occasions". "Londriniana" was the name given to this craft. The second document is a little-known, but quite accurate description of the manufacture of flock-leather wall hangings, which was included by the French academician, P. de la Hire, in his treatise on painting (8). While the subsequent notes offer an interesting picture of the diverse applications of the flocking technique, no mention is made in the eighteenth and nineteenth-century literature of the use of flocking on materials such as leather. On the other hand, already by the mid-eighteenth century, Fougereux des Bondaroy (9) lamented the decline in the use of leather in the manufacture of wall hangings, it having been replaced by cloth. There was a certain vogue for "tapisserie de tonture de laine" (i.e. fake tapestry produced by applying wool flocking on canvas or ticking), the production of which is described by Savary des Bruslons in 1742 in his *Dictionnaire Universel de Commerce* (10). Paper then rapidly became the most commonly-used material as a support for flock decoration, so that in 1756 the treatise of Dossie (11) expounds on the theme of flocking on paper for the production of wall-papers. Nineteenth-century literature is no less exhaustive on the subject, even though the technique appears to be used exclusively on paper (12).

Comparison of the sources brings out some common facts on the materials and techniques. Sometimes pigments the same color as the flocking are added to the adhesive — either an oleo-resin mixture or an animal glue — used to anchor the fibers to the surface to be decorated, in order to mask any possible imperfections on the flocked surface. Various methods are used to apply the adhesive:

- a) with a brush: this technique was commonly used before the introduction of wood-block printing and permits the creation of complex figured compositions with flocking of different colors (Savary);
- b) with a wood block: the design corresponding to the part to be flocked is cut in relief on the wood: the technique is the same as that employed for wood-block prints commonly done on paper and cloth. The use of several blocks, each reproducing a part of the design, makes it possible to create complicated compositions with different-colored flocking.
- c) with stencils: made of waxpaper, oilcloth or thin leather, the stencils are cut out where the pattern is to be flocked, pressed against the support and brushed over with adhesive. When removed, they leave an imprint similar to a printed one. This technique is quicker and cheaper than printing, but is not as precise. It lends itself exclusively to the transfer of simple forms, owing to the easy deformation of the materials used to make the stencils.

The flocking, usually obtained from silk or woollen cloth, undergoes a series of preparatory treatments; the fibers, de-greased and dyed in various colors, are first ground and then sifted through increasingly fine sieves until a homogeneous and finely-divided powder is obtained. The powder is distributed over the surface to be flocked, by hand or with sieves, and pressed lightly to anchor it to the adhesive. Excess fibers are removed with a soft brush. The velvet produced can be painted with tempera paints to add light and shadow to the uniform tonality of the flocking. The pigments are applied to the fibers with techniques similar to those used for spreading the adhesive: with a brush (Savary) or with a wood block (Le Normand-Figuier).



Fig.2) Wall-hanging in gilt leather, with flocking, of the Chapel.

2. The Flocked-leather Hanging of the Chapel

2.1. Assembly Techniques

The hanging is composed of vertical "panels", obtained by the assembly of numerous rectangular pieces of leather (skins) 86 x 51 cm, alternating with thin strips, 6 cm wide, which also function as a frieze at the base and top of the hanging itself. Four narrower vertical "panels", 33 cm wide, are inserted at the corners of the chapel. (fig.2). The skins that make up the vertical "panels" are sewn to each other, whereas the smaller pieces making up the thin strips and corner "panels" are merely glued together. All the main elements of the wall hanging—"panels", corners and narrow strips - are sewn to each other. The attachment to the wall with nails is not original.

2.2. Technique of surface decoration and ornamental motifs

The leather of the wall hangings is gilded with the traditional technique, i.e. "gold varnish" on metal leaf.

The flocking, originally red and now an ochre color, is applied on the vertical and corner "panels" according to a precise design and is anchored to the support with a layer of red-brown adhesive. The gilt background is stamped with punches. The vertical "panels" are decorated with plant motifs, involving intertwined shoots of leaves and flowers with a pomegranate at the center, a common motif in the design of fifteenth and sixteenth-century velvets (fig.3).

The corner "panels" are decorated to suggest columns, with punched shading on the sides: oak branches laden with acorns spiral up the shaft to the base of the capitals where the Chigi family coat of arms is painted in oil colors on a field of blue and red (fig.4). The strips, simply gilt, are punched in geometrical designs, predominantly the herringbone.

The skins of the vertical "panels" were decorated prior to assembly, the pieces forming the strips and the corner panels afterward.

2.3. State of conservation

a) support (fig.5):

- accentuated, localized deformations of the leather, probably caused by water infiltrations;
- stiffening of the fibrous tissue of the leather on the badly deformed "panels";
- rips, tears and other damage of a mechanical nature of light and medium extent, found principally where the parts are sewn, glued and nailed; this damage is due both to tension induced by contraction of the leather at points of attachment and to incorrect handling of the hanging as it was being mounted, dismantled and re-mounted;
- repairs of missing pieces with fragments of the same or other hangings;

b) decorative layers (fig. 6):

- total change in the coloring of the fibers from red to yellow (13);
- abrasion and loss of the fiber layer: accentuated, localized;
- loss and detachment of the adhesive layer and the metal leaf: accentuated, localized.

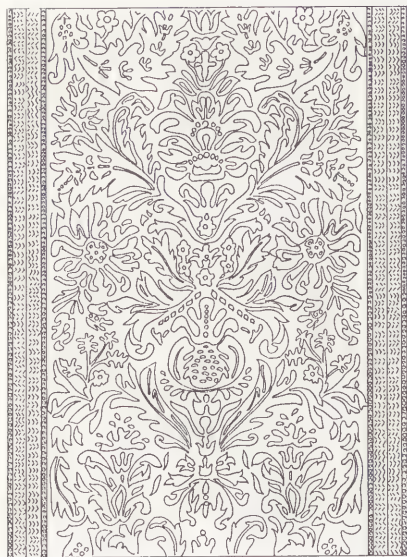


Fig.3) Decorative motif of the vertical "panels" and strips.



Fig.4) Decorative motif of the corner "panels".

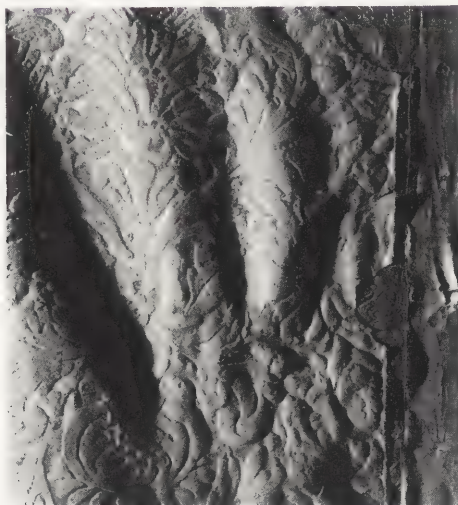


Fig.5) State of conservation of the support: localized deformation and repairs.

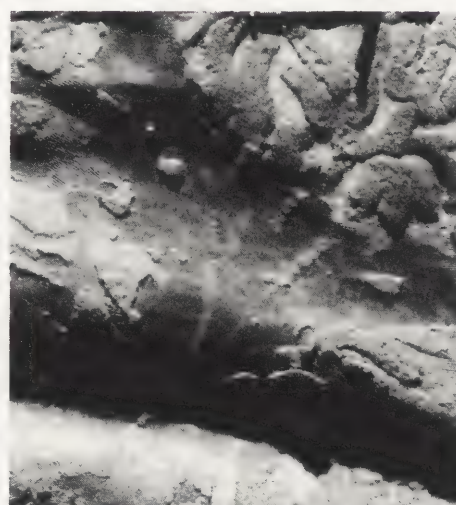


Fig.6) State of conservation of the decorative layers: abrasion and loss of flock.

Traces of insect erosion are visible on the flocked surface. The damage is found in limited areas over the entire hanging.

2.4. Studies

A first group of studies was carried out to identify and characterize the constituent materials. The results are summarized in Tables 1 and 2.

TABLE 1

Identification of the number of layers and their thickness - Cross section

Layer	% of total thickness*
Leather	87
Adhesive of metal leaf	1 <div style="display: inline-block; vertical-align: middle; margin-left: 10px;"> ≈ 0.1 ≈ 0.2 ≈ 0.7 </div>
Metal leaf	
"Gold varnish"	
Adhesive of flocking	12

* Total thickness: $1,4 \div 1,8$ mm (fig.7)

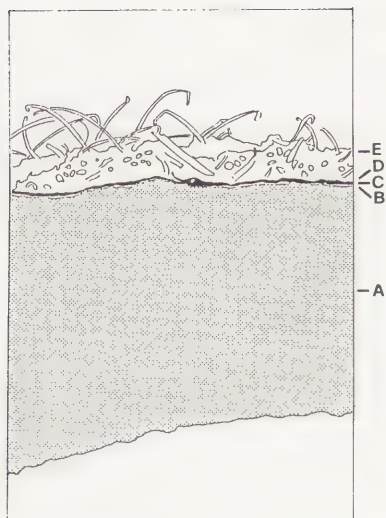


Fig.7) Cross section:
A) leather, B) adhesive of metal leaf,
C) metal leaf, D) "gold varnish",
E) adhesive and flock.

TABLE 2

Characterization of constituent materials - Microscopic examination and other studies

Tannins	Turkish Gall (14)
Flocking fibers	Wool
Fiber dye-stuff	Kermes/Cochineal (15)
Adhesive pigments	Red ocher

3. Conclusion

The work on the wall hanging of the chapel is part of a program including all the leather hangings that decorate the Chigi Palace at Ariccia.

Considering the richness of the documents in the Chigi archives, the authors of these notes intend to continue with research on a technical lexicon, which could eventually be compared with others of similar kind (16). Given the variety of wall hangings, we would also hope to make a substantial contribution both to the characterization of the constituent parts and techniques of execution of this type of artifact, and to the study of suitable methodologies of intervention and maintenance.

Problems of treatment of the decorative layers will be given closer attention, especially with regard to consolidation and cleaning. The flocked leather will receive special attention, as it involves a technique that has received little study to date.

Last but not least, our analysis will be aimed at evaluating the interaction between the support and its overlying materials — organic and non-organic — with the aid of spot registration of environmental conditions. These registrations should assist in establishing a standard system to control the behavior of the decorated leather in the course of thermohygro-metric fluctuation.

Acknowledgements

The authors would like to thank Cynthia Rockwell for her help in translating this report into English and preparing it for publication

NOTES AND REFERENCES

- 1) On the historical vicissitudes of the palace, see F. Petrucci, *Palazzo Chigi ad Ariccia* (Ariccia: Arti Grafiche Ariccia, 1984)
- 2) There are payments to Father Agostino of Gubbio and a boy employed "a lavorare li corami che sua Eminenza ha fatto fare all'Ariceia" (to work the leather /hangings/ that His Eminence has had made at Ariccia) and Gio. Garofalo who "li ha aiutato di issar li corami" (helped them to hoist the leather hangings). Biblioteca Ap. Vat., MSS Arch. Chigi 2619 ff.109-110, and 998 f.95.
- 3) Biblioteca Ap. Vat., MS Arch. Chigi 1090, f.193.
- 4) "Uno parato di corame d'oro con cimatura rossa fatto a broccatelli d'oro di pelli n 62 con sua frangia dell'istesso corame da capo e da piede in ca (canne) 36, che fanno pelli n 12 e n 4 colonnette con l'arma di S.E. da capo, venuto da Roma" (A wall hanging of gilt leather with red flocking worked like gold brocade, using 62 skins, with a frieze of the same leather above and below of 36 ca (1 ca = 2.234 m), which total 12 skins, and 4 small columns with the coat of arms of H.E. on the top, brought from Rome). Biblioteca Ap. Vat., MS Arch. Chigi 2898, f.234.
- 5) For a brief history of the technique, see especially:
 - C. Homan - J. Hamilton, *Wall papers* (London: Sotheby publication in association with the Victoria and Albert Museum, 1982), introduction.
 - J. Waterer, *Spanish leather* (London: Faber and Faber Ltd., 1971), 61-63.
- 6) See: T. Rymer, *Foedera...* (London, 1732), vol. XIX, 554. The patent is dated 21 May 1634.
- 7) J. Beckmann, *History of invention, discoveries and origins* (London: H. Bohn, 1846), vol. II, 379-85.
- 8) P. de la Hire, "Traité de la pratique de la peinture" in *Memoires de l'Academie Royale des Sciences depuis 1666 jusqu'à 1699* (Paris: Par la Compagnie des Libraires, 1730), vol. 9, 637-730.
- 9) Fougeroux de Bondaroy, *Art de travailler les cuirs dorés ou argentés* (Paris, 1762), 1-6.
- 10) J. Savary des Bruslons, *Dictionnaire universel de commerce* (Genève, 1742): Articles: "Tapisserie de tonture de laine" and "Papier velouté". The former article reappears virtually intact in the *Enciclopedia* of Diderot.
- 11) R. Dossie, *The Handmaid to the arts* (London, 1758), vol. II, 422-426. Another eighteenth-century source: J.B. Papillon, *Traité historique et pratique de la gravure en bois* (Paris, 1766), vol II, 535-536 and Supplement, 95.
- 12) L.S. Le Normand, *Manuel du fabricants d'étoffes imprimées et de papiers peints* (Paris: Roret, 1856), 187-192.
- 13) Microscopic analysis reveals rare occurrences of red fibers.
- 14) M.C. Berardi, *Identificazione dei tannini nelle conce antiche*, report I.C.P.L. — attività 1988, unpublished paper.
- 15) Investigations are still going forward.
- 16) In Italy, a sample study has been conducted on archival documents from Florence and Urbino: F. Scalia, "L'arte dei corami. Appunti per una ricerca lessicale", in *Atti del Convegno Nazionale sui lessici tecnici tra Seicento e Settecento*, Pisa: 1980 (Firenze: Eurografica, 1981), vol. II, 357-384.

ABSTRACT

This paper describes the conservation of three related objects which were made to come within the discipline of 'textile conservation' for treatment. This is essentially a practical paper and the intention is to describe some 'skin'-related objects which may not come within the scope of leather conservators generally: to discuss the problems these posed and to describe in detail how these problems were solved using techniques and treatments which were drawn from several conservation disciplines.

The three objects were made from horsehair, bear skin and ermine.

KEYWORDS

HORSEHAIR HAT, BEARSKIN BUSBY
ERMINE-LINED CAPE, FUR/HAIR.

A 1740's HORSE HAIR HAT, A BUSBY c1827 AND A FUR-LINED CAPE c1936

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Introduction

It often falls to the textile conservator to deal with objects outside his/her direct material discipline.

Textile objects are often composed of many differing materials; sometimes ivory, bone, metals and glass are incorporated, often textiles are painted and sometimes textiles are made almost entirely of straw, paper feathers, leather or hair, and yet still come under the heading of 'Textiles' and are presented to the textile conservator for treatment.

Here are described three such objects, all 'textiles' but all made from and using materials related to skin or hair.

The objects range in date from 1740 to 1936 and are described in chronological order.

Hat of Horsehair and Wool Braid c.1740 (T273-1982)Examination

This hat is made from a coarse braid made from horsehair and wool, woven like a fancy ribbon and stitched together in a spiral to form a large disc.

The shaping of the crown is achieved by a row of gathers stitched to mark the point where the brim and the crown meet.

The hat was in a very poor condition being without its wire support or any lining, decorative trimmings or ribbons. Very few of these hats survive; there were none similar of this material in the Museum collection; so although in an appalling state it was an important object and historical document. (See Fig.1)

The hat had come into the collection with a number of other objects and had lain for many years uncatalogued and unidentified. It had come to light by chance. It had been folded in half then concentrated to form a squashed, gathered-up shape which bore no obvious resemblance to a hat at all.

It was a grey-brown colour due to surface grime and felt slightly sticky. Many of the rings of spiral braid had become unstitched. The outside braid forming the brim edge was splitting throughout, the weft of the braid had degraded and broken forming radiating lateral splits.

The hat was measured and a simple stand was made to support the hat during examination and treatment. A cardboard disc was cut with a diameter slightly larger than that of the hat. A circular hole was cut in the centre to enable the card to fit over a wooden head stand. A wedge was cut from the card and the space re-joined to give an angled-down brim shape. The head stand was covered with polyethylene and so was the card shape. The card was then fitted over the head to complete the stand.

The hat, although damaged, could be handled quite safely. It was put onto the stand so that more detailed examination could take place.

Once on the stand the line of gathers marking the position where the brim and crown meet could easily be seen. There was an oblique line of raw-edged holes around one side, the arrangement of which indicated stitch marks or fixing points for heavy trimmings (possibly artificial flowers or ribbon rosettes). These holes were examined under magnification and were seen not to be insect damage, insect holes are quite different. The braid was examined through a Kyowa binocular microscope using reflected tungsten light and a fibre optic light source, at magnifications ranging from 10X to 90X. The heavy deposits of dirt and dust particles on the braid could clearly be seen at 50X magnification. Photomicrographs were taken of this for later comparison. Photomicrographs were taken of the splits so that damage to the edge could be monitored and compared before and after cleaning.

There were two further small raw-edged holes on opposing sides of the brim. These were thought to be fixing points for ribbons. A silk hat of almost the same date and similar style was examined for comparison to verify this supposition.

The silk thread used to stitch the braids together had rotted and dusted away in many places causing the bands to separate. The first thing to do was to re-sew the braids together to give cohesion of structure. This was done using 'Mara' polyester thread by Perivale Gutermann in decitex 400(3) metric count 70(3).

Cleaning

The second problem was to clean the hat. A small area of the brim was tested for washing by swabbing out onto blotting paper with deionised water and 1% Lissapol, a non-ionic detergent.(1) Dirt was released onto the blotting paper below but not enough to give the desired visual improvement to the hat.

A second patch test was carried out using 10% glycerol in deionised water as a pre-treatment. This was left for approximately 20 minutes then the test with washing solution was repeated on the pre-treated area. Far more dirt was released onto the blotting paper and the appearance of the area was much improved. (See Fig.2.)



Fig. 1
Hat of horsehair and wool
braid c.1740 (T273-1982)

Before conservation

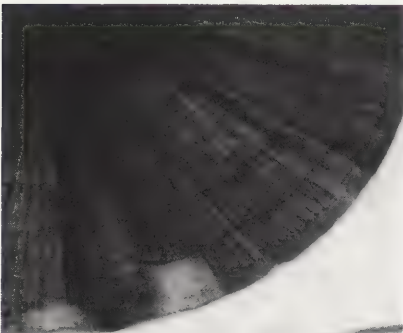


Fig. 2
Hat of horsehair and wool
braid c.1740 (T273-1982)

Patch tests prior to washing
using non-ionic detergent
and glycerol pre-soak and
detergent.

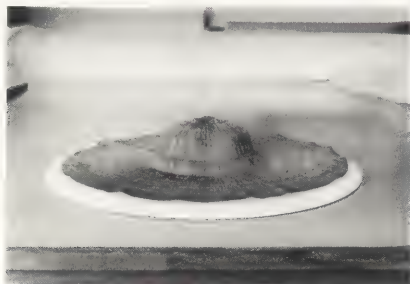


Fig. 3
Hat of horsehair and wool
braid c.1740 (T273-1982)

After conservation



Fig. 4
Busby c.1827 (Loan 44-51)

Before conservation

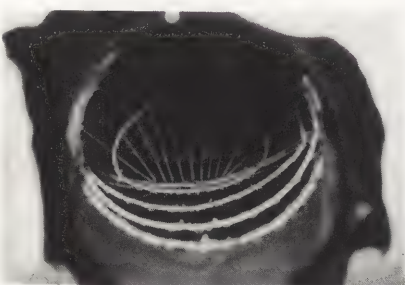


Fig. 5
Busby c.1827 (Loan 44-51)

Interior view showing
construction

The hat on its support stand was set on the washing table and the hat thoroughly wetted out by swabbing with the 10% glycerol solution. It was left to soak for 30 minutes then the hat was washed.

The washing solution was poured over and agitated using a soft mop-headed paint brush working in a circular motion over the complete hat. The hat was rinsed with deionised water applied by a hand spray. Washing and rinsing were carried out three times. The hat was lightly blotted using absorbant paper then left to dry naturally.

The hat looked clean and no longer felt sticky. It was again examined through the microscope. The surface deposits had almost all gone leaving only a few scattered particles. The splits and edge-damage were examined and no appreciable worsening of this condition could be detected. The splits did not seem to have opened further at all. Photomicrographs were taken to record this.

Support

A support method now had to be chosen for the damaged braid. It was decided that a thermoplastic adhesive technique was the most appropriate. The carrying fabric had to be very flexible and easily mouldable to the hard surface texture of the braid. For this reason a woven fabric with a definite grain and weave structure was ruled out. Nylon gossamer laminating tissue, a welded fabric based on 'Cambrelle' heterofilament nylon by I.C.I. Fibres was chosen.

The adhesive also had to be flexible yet strong. It should have no tendency to peel off the hard shiny horsehair braid over the passage of time and with handling.

Mowilith DMC 2 (R) polyvinyl acetate emulsion was the usual thermoplastic adhesive used in the Textile Conservation Department in 1984 when this hat was conserved, but it was felt that this would not be strong enough to hold onto the shiny smooth horsehair, and withstand handling.

Texicryl 13.002 (R), an acrylic co-polymer was chosen as an alternative. It had been used previously for fixing fabric to a smooth shiny surface. (2)

The nylon tissue was dyed to a colour to match the hat using Tectillon a "level dyeing" acid dye for polyamides by Ceiba Geigy.

It was then treated with a 50:50 solution of Texicryl in deionised water painted out as a film onto polyethylene sheet.

When dry, the polyethylene was peeled away and the film treated tissue was ready for use. A strip was cut and ironed onto the back of the damaged outside ring of braid through silicone release paper using a spatula iron set at 80°C. The hat had been turned upside down and was supported in a substantial ring made of tissue paper to facilitate easy access to the underside of the braid.

The Texicryl film held well and showed no signs of peeling away from the horsehair even with a gentle tug. The excess of the cut film strip was trimmed back to the edge of the brim to give a clean finish.

The holes were repaired using the same method.

At the time of conservation it was decided not to make up the hat with a replacement wire support, ribbons and trimming as it was not then required for display, so a support storage stand was made.

Measurements were taken from the hat and a six-segment card dome was constructed. The dome was covered with a layer of polyester wadding cut to shape, and a tailored cover of cotton lawn was pulled over this and sewn down onto a padded cotton lawn covered card circle, slightly larger than the brim. The hat was placed on this stand and returned to store. (See Fig.3.)

In 1989 it was decided to use the hat for display and it was returned to the conservation department for the final reconstruction and trimmings. The adhesive-supported band was examined and found to still be holding well with no signs of springing off, peeling or discolouration of the adhesive.

Busby c.1827 Worn by 1st Duke of Wellington: Part of Colonel of the Grenadier Guards Uniform (Loan 44-51)

In 1988 it was decided to refurbish the costume case at the Wellington Museum Apsley House London, housing four costumes worn by the 1st Duke of Wellington.

Amongst these was his uniform worn as Colonel-in-Chief of the Grenadier Guards.

The costumes had not been cleaned or examined since 1953.

Apsley House is situated at Hyde Park Corner, a busy and traffic-polluted area of central London.

The rooms at Apsley House are not air conditioned and the case in which the costumes were displayed was unsealed. The case showed the deposits of atmospheric dirt and dust that had built up over 35 years.

The busby and uniforms were filthy. (See Fig.4.)

Examination

Busby's are large and imposing and though they appear to be extremely heavy are not so. Every part of their construction is designed to minimise the weight and make them comfortable to wear.

The busby was constructed over a substantial cane support, the ribs of which were lashed together with split cane to hold them securely. (See Fig.5.)

This was set onto a band 12cms deep of stiff felted material which forms the part which fitted over the head. The bottom edge of this was covered in a brown velvet band and a small leather peak projecting only 3cms was stitched onto the front just above the velvet band. The whole structure was covered in thick coarse dark brown fur 9 to 10cms long.

A quilted lining, with drawstrings for size adjustment, was sewn to the velvet band and pushed up inside the busby. On the outside was mounted a lightweight copper gilt military badge. There was also a leather strap and a hollow copper gilt chain link chin strap mounted on brown velvet.

The badge was damaged, the small central crown being broken off and caught in the fur. The badge and fragment were removed and taken to Metalwork Conservation for repair. To the left side of the busby was a dirty grey horsehair plume set above two gilded wire tassels. By examining the plume at the root it was apparent that it had originally been white.

Busby's are also known as bearskins, so before proceeding with the cleaning and conservation I wanted to confirm that it was really bear fur.

During handling a few hairs had fallen away and these were collected and examined through a Leitz Orthoplan microscope using tungsten light at up to 320X magnification. There were three types of fibre present, a fine crimped wool, a fine fibre partly straight and smooth, and finally a coarser hair, smooth along its length. Permanent mounts of scale casts were made and photographs taken. The samples were identified as from the genus *ursus*-bear although no clearer identification was possible.

Conservation

The busby was set upon a wooden head stand for further examination and treatment. The hair was dull, dry and felt sticky, with a black dust all over which came off on one's hands at the slightest touch.

The fur was otherwise in good condition and the skin was sound and supple. The black dust had not penetrated through the hair as far as the skin so this was still clean.

There was a little moth damage in places but the infestation seemed to have been inactive for some time leaving only dried-up cocoons matted into the hair. These were picked out with tweezers and the frass removed locally by brushing and by vacuuming using a vacuum tweezer unit. (3)

I was confident that the hair could be cleaned using an aqueous treatment but as the skin was probably prepared by alum tawing, care would have to be taken to keep the skin dry, as wetting might cause hardening of the skin. (4)

A test was made at the bottom of the busby to determine the best washing procedure for the hair.

A small section of hair would have to be treated at a time, working in layers around the busby starting at the bottom and working up to the crown.

Each tuft was swabbed out onto white absorbant paper to soak up the dirt. The paper was repeatedly changed throughout the rinsing for maximum water removal and to monitor when the hair was clean. The surrounding hair was pinned back to keep it out of the way, using stainless clips. Firstly, each tuft was swabbed out with deionised water, working away from the roots towards the hair ends, ensuring that the skin at no time became wet.

A 1% solution of non-ionic detergent was then applied (1) and worked through the hair with a cotton wool swab. Deionised water was then swabbed through to remove the detergent, followed by a mixture of 50:50 industrial methylated spirit and deionised water. This mixture was used to help release any remaining dirt and see if further washing was necessary. Finally, the tuft was swabbed out using industrial methylated spirits alone, to help remove excess water, then blotted dry with absorbent tissue. The tuft was combed and allowed to complete drying naturally whilst the next section was treated.

This method was also adopted for cleaning the horsehair plume.

To wash the whole busby took approximately seven days. The improvement in appearance was remarkable, the hair now felt soft and springy and looked lustrous and beautiful. The horsehair plume was white and glossy again.

Now that the hair was clean, attention could be given to the trimmings and lining.

The trimmings were swabbed over using industrial methylated spirits to remove the surface dirt and dust.

The lining was made from a tube of silk, the bottom 7cms was quilted in lines through onto a woollen padding. The top 7cms was finished with a gathering channel so that it could be pulled up to make an inner crown which would fit snugly onto the head. There was a second channel at the join between the quilted and plain silk with a gathering ribbon running through which could be pulled up for further fit-adjustment.

The lining was dirty, showing ingrained staining from head grease, perspiration and general wear. The silk was degraded and shattering, and as the lining was almost detached from the velvet band it was removed for cleaning and conservation.

It was solvent-cleaned in a tray, in a fume chamber, using 1.1.1 trichloroethane Genklene (R). Three changes of solvent were used.

It was decided to support the shattered silk by mounting it onto a thermoplastic adhesive treated film. This would only suffice for the unquilted area as there was no means of access for the support to the back of the quilted silk. Silk crepeline was treated by painting it out onto polyethylene with a 20% solution of Mowilith DMC2 in deionised water. When dry this was peeled off and ironed onto the back of the shattered silk using a



Fig. 6
Busby c.1827 (Loan 44-51)

After conservation

spatula iron set at 80°C. The first line of quilting and a line of stitching forming the secondary channel were unpicked to allow access for the crepeline film.

The whole of the lining was now covered in untreated silk crepeline to support the quilted area and to give the protection and extra strength to the already supported silk for when the hat was on display again.

The unpicked stitchline was re-worked using Skala^(R) polyester U151 monofilament thread by Perivale Gutermann, and the gathering channels re-made. A new ribbon was inserted into the secondary channel and both channels were pulled up and the ribbons tied. The conserved lining was stitched back into the busby using 'Mara' polyester thread.

The copper gilt badge was re-stitched onto the busby using a heavy linen thread similar to that originally used. (See Fig. 6)

A Blue Felt Cape With an Ermine-Lined Hood 'Vive La France' by Paquin. French 1936 (T123-1980)

In preparation for the Paquin exhibition to be held in Lyon in 1990, this object was brought to the Conservation Department for cleaning before being sent out on loan.

Examination

The cape is made from blue wool felt and is approximately 73cms long. It is lined with white felt and the hood is lined with ermine, with an ermine tie at the neck.

Tests were not necessary to identify the fur as the cape is well documented and has its Couture Number 50467 stamped on the back of the Paquin label which is stitched in at the neck.

The cape was in good condition apart from a few small moth holes, but grubby from wear. The ermine hood lining, however, had not fared so well. It was grubby but also damaged. In some places the skins had started to split and in two areas of particular damage they had shredded into small fragments. (See Fig.7) At some time these areas had been stuck down to the lining and the adhesive had now become hard. Fortunately, the adhesive had not soaked through the skin or impregnated the fur itself.

Conservation

The hood and ermine tie were unstitched from the cape and the cape was sent to a commercial dry cleaners for solvent-cleaning with perchlorethylene.

Before any treatment could be carried out to the hood it was necessary to unpick and release the silk lining from the back of the skins. This was not unpicked entirely but only where necessary to gain access to the damaged parts.

Fortunately, the adhesive used to stick the damaged areas was soluble in acetone and was easily removed by localised treatment using small cotton wool swabs soaked in acetone, and a scalpel blade used for scraping away the softened adhesive from the back of the skin.

The general condition of the skins appeared to be good; they were not dry or brittle, but there was marked yellow staining in the damaged areas and particularly in these parts there was little tensile strength.

The damaged areas corresponded to the neck and ear regions when the cape was in use and the hood draped over the head, and it was possible that the owner had sprayed herself with perfume and these stains could be directly attributable to this. Could the alcohol or some other ingredient in the perfume have caused a rapid oxidation of the fat in the skin and caused this shredding condition, known to taxidermists as 'fat burn'?

The rest of the skins seemed to be strong and were not stained.

As the fur was generally grubby and had some lipstick marks, it was cleaned by swabbing over with white spirit BS245^(R), working with the direction of the hair and swabbing onto blotting paper. The fur was well blotted then left to dry. It became much cleaner after the treatment but the lipstick marks could not be removed.

The next problem was how to repair the shredded skin. Obviously an adhesive treatment would have to be used but it would need to be very flexible to be compatible with the skin. Possibly a thermoplastic adhesive would be necessary but the heat setting temperature would need to be low so as not to damage the skin. If a contact adhesive were used it would need to dry speedily to prevent slipping and must not seep into the skin. Similarly, a light and flexible support fabric would be necessary to carry the adhesive.

Nylon gossamer was chosen as the support fabric and as the skin was white it was unnecessary to dye it to match the colour of the skin.

An experiment was carried out to assess the merits of two adhesives which I thought may be suitable.

Mowilith DMC2 had already been considered and thought to be unsuitable as I did not feel that it would give a good enough surface adhesion to the skin when used as a light film.

Beva 371^(R) film, a thermoplastic adhesive and silicone adhesive SF2^(R) a contact adhesive were chosen for the experiment.

A piece of white rabbit fur was taken and cuts made in the skin with a sharp scalpel. A small square, 5mm x 5mm, was painted with silicone adhesive FS2 on either side of one of the cuts, and a small strap of nylon gossamer,

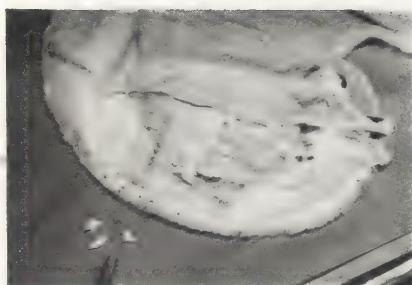


Fig. 7
Ermine lining from Paquin
cape (T123-1980)

Showing damage to the skins

approximately 5mm x 10mm, was pressed onto the adhesive, pulling the cut together and effecting a precise joint.

The joint held firmly, there was no slipping and the adhesive did not creep into the surrounding skin, neither did it penetrate through to the fur side of the skin.

When quite dry, after about 20 minutes, the skin was manhandled to test for flexibility: this was most satisfactory. I then tried to peel off the patch. It would not easily come away.

A small sample of Beva 371 film was prepared by ironing it onto a square of nylon gossamer between two sheets of silicone release paper. A small strap approximately 5mm x 10mm was cut and ironed onto a second cut in the rabbit skin, through a piece of silicone paper. A spatula iron, set at approximately 70°C-75°C, was used.

A precise firm join was effected. The adhesive did not creep or migrate into the surrounding skin, neither did it penetrate through the skin to the fur side.

The skin was manhandled to test the flexibility of this repair and it too was most satisfactory. I then tried to peel off the Beva-treated patch and it would not come away easily.

I then compared the two repairs visually. The SF2 repair had slightly darkened and although the Beva 371 could be seen, it was barely perceptible in comparison.

The Beva 371 film was therefore chosen for the repairs.

A 15cm square piece of Beva 371 film applied to nylon gossamer was prepared as previously described.

The damaged hood was laid out on a board and the shreds of skin were held in alignment using fine entomological pins stabbed through into the board.

By ironing small straps of the Beva film onto each split, gradually the damaged areas could be re-pieced and made whole. (See Fig.8)

Because there were tufts of hair missing from the front, it could still be detected that there had been damage but the skin was again sound.

One side of the silk lining was particularly damaged so the original was laid back in place but covered with a replacement. This was made from jap silk dyed to match using Lanaset, a range of metal complex and reactive dyes by Ciba Geigy. It was stitched in place over the damaged side of the lining and the tacking lines holding the lining to the skins were reworked.

The ermine lining was now ready to go back into the hood. It was pinned in place using entomological pins and stitched using Mara polyester thread. The ties were stitched back in the same way.

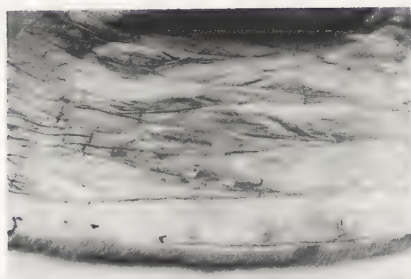


Fig. 8
Ermine lining from Paquin
cape (Tl23-1980)

Showing damaged areas of skin
after conservation.

Conclusion

In offering these three case histories I have tried to show how far the 'leather- and skin-related object' topic can be extended within the textile discipline and how diverse the treatments may be which are required to successfully deal with objects within this very demanding field.

Acknowledgements

The author would like to acknowledge the help of Miss Josephine Darrah, Senior Scientific Officer at the Victoria & Albert Museum, for preparing casts of scale patterns and cross-sections, and identifying the fibres.

References

1. Non-ionic detergent recipe:
1 gram per litre Lissapol N
0.1 grams per litre Sodiumtripolyphosphate
0.1 grams per litre Sodium Carboxymethyl Cellulose
2. The Mounting and Storage of Prints, Drawings and Watercolours at The British Museum by Eric Harding
Abstracts and reprints of the Conservation of Library and Archive Materials and the Graphic Arts Conference. Cambridge 1980.
3. DA7 Vacuum, Tweezer Unit supplied by C L E Designs Limited, see Materials List.
4. Guide to Leather Conservation by John Waterer, published by The Museum of Leathercraft.

Materials

'Mara' polyester thread by Perivale Gutermann in decitex 400 (3) metric count 70 (3). Perivale Gutermann

'Skala' Gutermann U151 polyester monofilament in decitex 150/1 metric count 65/1

Perivale Gutermann Ltd
Wandsworth Road, Greenford, Middlesex, UB6 7JS

All photographs courtesy of
the Trustees of the Victoria
& Albert Museum

Nylon gossamer laminating tissue, based on 'Cambrelle' heterofilament nylon by I.C.I. Fibres. Available from:

Picreator Enterprises Ltd
44 Park View Gardens
Hendon
London NW4 2PN

Mowilith DMC 2 (R) Polyvinyl acetate emulsion, co-polyester of polyvinyl acetate dibutyl maleate by Hoechst Chemicals available from:

Trubond Adhesives Ltd
Unit 2A
Govebell Industrial Estate
Wrecclesham Road
Farnham
Surrey GU20 4PL

Texicryl 13002 Acrylic co-polymer

Scott Bader Co Ltd
Wollaston
Wellington
Northamptonshire
NN9 7RL

Tectilon dye. A level dyeing acid dye for polyimides, by Ceiba Geigy.

Lanaset dye. A range of metal complex and reactive dyes by Ceiba Geigy.

Ceiby Geigy Ltd
Dyestuffs and Chemicals Division
Clayton
Manchester
M11 4AR

Genklene N (R) 1.1.1. Trichloroethane, a chlorinated hydrocarbon solvent.

Supplied by Hunting Lubricants & Specialised Products Ltd
Rainham Trading Centre
New Road
Rainham
Essex
RM13 8QT

Beva 371 (R) film available from

Archival Aids
Ademco Ltd
Coronation Road
Cressex Estate
High Wycombe
Bucks
HP12 3QU

Silicone adhesives SF 2 (R)

From: John G Shelley Co Inc
Art Sciences Division
16 Mica Lance
Wellesley Hills
Massachusetts 02181

Vacuum tweezer unit

Supplied by: C L E Design Ltd
69 Hodges Road
Wimbledon
SW19 1HQ

ABSTRACT

There is a striking difference between the traditional way of leather tanning and the modern leather tanning, in that the modern tanners use chemicals like sodium sulphate, sodium sulphate and sulphuric acid. Before 1900 these chemicals were not used in tanneries. The influence of these chemicals on the deterioration of vegetable tanned leather made before and after 1900, is explained with respect to a goatskin article tanned in about 1800 in Sudan, and since 1825 included in the collection of the National Ethnographic Museum in Leiden.

KEYWORDS

Pre-18th Century leather making, liming, bating, tanning, vegetable tanning, sulphurous substances.
Sudan, Netherlands.

SULPHUROUS SUBSTANCES IN THE TANNING OF LEATHER WITH VEGETABLE TANNINS

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While examining the condition of the leather, fur and feather collection at the National Ethnographic Museum in Leiden, my attention was drawn to a particular point of interest.

Objects made of vegetable-tanned leather, including many goatskin articles originating from the Sudan, seemed still to be in good condition despite the rather primitive conditions under which they had been kept in the depots. There was no trace of any form of red rot, the pH level was measured as 4.5, and tests for ammonium sulphate proved negative.

The objects had been brought to the Netherlands in 1825, and as already mentioned, the conditions under which they were kept, whether in storage or on display, were primitive. They had been stored in an attic which lacked any kind of climate-control, under a zinc-covered roof. The room was therefore subjected to extreme heat in the summer and cold in the winter, and to equally extreme differences in relative air humidity.

The leather used for these ethnographic objects had been manufactured circa 1800 in the Sudan, using only natural materials, and no chemicals.

Why is our modern-day vegetable-tanned leather so susceptible to the damaging effects of SO_2 ? It can be seen how our samples of new vegetable-tanned leather are being destroyed, and all attention had been focussed on the effects of the SO_2 in the atmosphere. Why, then, does this SO_2 seemingly have no effect on the leather from the Sudan, which was produced nearly 200 years ago?

The absence of ammonium sulphate means that no amino acids have been converted into ammonium sulphate, the end-product of the degradation process caused by SO_2 .

The manuscripts written by the gold leather makers of Mechelen also deal with the tanning of leather. On comparing their method of tanning with the present-day method, one's attention is drawn to the current use of organic acids and sulphur compounds. It is preferable to treat fresh skins immediately in the tannery, but this is almost impossible today, mainly because of the vastly developed world trade in skins. The consequence of this is that longer periods elapse between cleaning the skins and the actual tanning process, and care must be taken to prevent any rot setting in. This is done by preserving the skins by, for example, drying them. The gold leather makers of Mechelen describe this.* They also warn against allowing bacteria to take hold during the period of soaking in the tannery. The bacteria appear in the grain of the leather, causing small lumps half the size of a peppercorn. Nowadays, modern moisturizers are used which contain a bactericide.

In order to shorten the soaking time considerably, caustic soda, soda, sodium sulphide or sodium sulphate are used when soaking in an alkaline solution.

* Note a.

"As long as the skins (hides) remain in the drying lofts, they must be beaten each fortnight in August, when the weather is warm. In other months each third week".

* Note b.

"If one wishes to soften the skins, these must be immersed in the soaking pit and lie there for eight days. One must be careful that the water in the pit does not get dirty, as otherwise the bacteria would degrade the skins. After the soaking the skins must be rinsed well with water, as otherwise the skins will start to rot".

The principal aim of these processes is to return the skins to their natural state.*

Nowadays amines are added to the liming bath. In this way the removal of hair from the hides is speeded up, without an excessive swelling of the hides.

The first soaking of the skin removes most of the hair, while the second treats the collagen fibres, and loosens the interfibril texture of the skin, preparing it for the actual tanning process, and ensuring a better binding of the tannin.

The Mechelen gold leather makers were already aware of the dangers of calcium carbonate formation, which they referred to as "lime stains". It forms very readily on the skins if they are left unprotected from the sun and air. Affected patches will not take up the tannin so easily, and will become hard and acquire a yellowish-white colour. Furthermore, the fibres will break very easily later on. Such patches in the leather can be removed only with a highly concentrated acid, e.g. hydrochloric acid. The gold leather makers did not have access to such strong mineral acids in their day.

The skins are removed of their hair and excess fat, and any remains of flesh. This used to be done on a beam, using a fleshing knife, as depicted in numerous prints. These days a machine performs this function. It is important to remove as much lime as possible from the surface and the capillaries, in order to avoid the formation of insoluble calcium carbonate, especially when using hard water, water with temporary hardness (containing bicarbonate) or water containing a lot of soluble CO_2 . Intense deposits of calcium carbonate can occur within the fibres of the skin, resulting in permanent hardness. Sometimes the tannin cannot penetrate, and patches of untanned skin remain, particularly on the grain and seldom on the flesh-side.

The gold leather makers used the initial liming only in removing the hair. The collagen fibres were treated during the second soaking, and the interfibril construction was loosened. In order to shorten this process, numerous chemicals are nowadays added, e.g. sodiumsulphite, calcium sulphide or sodium sulphur hydrate, with sodium sulphhydrate in combination with calcium chloride.

* Note c.

"The skins are immersed for $1\frac{1}{2}$ hour in the liming pit with fleece upwards. Over each pack of 25 skins is strewn a shovelful of lime "i.e. over the upper fleece".

* Note d.

"During the preliminary liming the skins should not be kept in the liming pit for longer than 8 days; 14 days to 3 weeks is the utmost limit. By then the hairs should be loose enough to allow "depilation".

* Note e.

"One should instruct the workmen who are busy with depilation, to "do this well. One also should pay attention that the flesh side of "the skins is up, as otherwise the sunlight can damage them. And if "the workmen take a lunchbreak, they should, before that, protect "the skins against the sun by covering them with sacks or mats".

* Note f.

"For a complete liming the skins must remain in the pit for 6 to 8 "weeks. In the winter, three months. One can test whether the skins "are full (swollen). In that stage one can remove flesh from the "skin with a finger. One should take care that the lime is a paste " without lumps".

* Note g.

"One must take care that the skins could lie in the river for at "least 2 or 3 flood periods.

"(In Mechelen (Belgium) the river "De Delen" was connected with the "sea, hence the tides and the floods). After that the skins must be "submitted to scudding".

The afore-said gold leather makers reported that the hides were done, that is fat and flesh discarded, if they had lain for a while (1 or 2 flows) in the river.* The gold leather makers point out that also here one had to be cautious for the formation of calcium carbonate. In order to avoid such contamination the hides were kept under water. At present, the problem of the formation of calcium carbonate is normally resolved by the use of sulfonic or lactic acid.

After liming and depilation, followed the bating. In this process the excessively swollen hides were submitted to a moderate shrinking by way of weak organic acids as well as to enzymatic degradation, both found in abundance in animal dung. Fowl and dog dung were commonly used for the purpose. During bating the hides were purged from loose collagen fibres and were thus rendered supple, yet thin. As the optimal activity of the enzymes took place at about 37°C, the gold leather makers carried out the bating procedure with warm water.

The gold leather makers brought the bating to an end by immersing the hides in cold water overnight. Nowadays the bating is terminated with either common salt or sodium sulphate or with the following chemicals: hydrochloric acid, sulphuric acid or formic acid. With these chemicals, the pH \pm 7,8 in the bating stage is reduced to pH 2,8 or pH 2,5.

However, such chemicals were not used before 1900. In old leather made before 1850 these chemicals are, therefore, absent. Because of that, the pH of such leather is never lower than 2,8, and that is entirely due to the tannin extracted from chesnuts, the pH of which is 2,8. Vegetable tanned leather cannot have a pH lower than 2,8, and if it does, the low pH is attributed to the deposition of air-pollutents such as sulphur dioxide and sulphur trioxide or to the remnants of sulphuric acid and sodium sulphate, which have been used to stop the bating.*

* Note h.

"One must avoid that the skins lie in the river during the tide period. During these intervals the skins should be kept in "barrels".

* Note i.

"The skins must be rinsed with water very well, so that no lime rests remain in the skins".

* Note j.

"After scudding the skins are submitted to bating. The day before or on the same day a mixture is made of the dung of dogs, the quantities of which is known to us. One should take care that bating is carried out always in the same barrel".

* Note k.

"After bating the skins are kept in cold water until they are transferred to the tan drums. Before tanning the excess of cold water and dirt must be removed from the skins, as otherwise both the temperature in the tan drum will be depressed and the tan drum will be polluted".

* Note l.

"On the day of tanning the water in the tan drum is made warm by the addition of warm and lukewarm water. The temperature of the water in the tan drum must be fixed very precisely, as if the water is too warm, the grain of the skins would shrink and peel off. Such skins are useless".

"For the purpose of the first drum rotating 2 or 3 quantities of ground bark are put in, the drum. After one day long rotation, if the tanner can afford it the drum is allowed to stay immobile for several days, otherwise for only one day".

"For the second drum rotating 4 quantities of finely ground bark are put in the drum. After one day long rotation, the drum is allowed to stay immobile for several days".

"For the third drum rotating 5 quantities of finally ground bark are put in the drum. One day long rotation is followed by three days immobility".

The vegetable tannins are made up of molecules ranging greatly in size and containing many phenol groups. They react as acids and they join with the base NH_2 groups contained in the skin to form a salt, which we can call leather. A large part of the vegetable tannin binds by absorption and adsorption.

The later development of chrome tanning is similar to the vegetable tanning process with regards to its technical application, at least the way the gold leather makers applied it. The process takes place in a revolving vat, the depilated skins being constantly turned in the tanning solution. In this way the whole of the skins are treated, and not just their outsides. The tannin particles are small enough to be deposited easily in the skins. The gold leather maker too gradually adds more of the tanning solution to the vat. He would tan leather 3 to 5 days for skin leather, and at least 3 weeks for leather with a thickness up to 1.5 mm. Chrome tanning can be completed in 8 hours. When the tanning is finished, the pH of the leather should be between 4,1 and 3,5 preferably 4,1 to 5.*

The tanning process is now over for the maker of gold leather. He mentions nothing in his writings about greasing the leather, something in common practice today.

Comparing the modern process with the old-fashioned method of tanning, it is noticed how many chemical substances have been introduced to speed up the process. It is inevitable that the addition of the various substances should have an effect on the resulting leather, particularly on the durability of the finished product. Considering that the leather from Africa has been exposed to our atmosphere since 1825 and yet shows no signs of degradation in the form of ammonium sulphate, we may conclude that the problem with our modern-day leather for use in restoration were initiated at its manufacture.

This does not rule out any possibility of damage being due to increased levels of SO_2 in the atmosphere, but it is well to draw attention to the modern methods of tanning leather with vegetable tannins.

The Central Research Laboratory and the Royal Librarian in The Hague are commissioning the manufacture of leather using the late 18th century method described here, excluding all use of sulphurous substances and chemicals.

The aim is to produce leather with good durability, (suitable for use in restoration).

* Note m.

"The skins must be tanned well. After that they are rinsed. This helps in stretching them out. Once being outstretched, they are brushed off, and are further outstretched until they become "flattened. After that the skins are cut in quadrangles, or if necessary, in breadths".

Translated by Miss C.J. Witterick.

Consulted works:

1. Het Mechelse handschrift, het zogenaamde secreteboek van Schoone diversche ende eerlijcke konsten werd geschreven door drie goudleer makers uit Mechelen Jan Vermeulen (1677) Carolus Jacobs (1711) en Jacobus Versluysen (1783). Het bevindt zich in het Stadsarchief van Mechelen (handschriftenverzameling).
2. Ir. P.J. van Vlimmeren, Chemie van de Lederbereiding, Waalwijk 1955.
3. W.B. van Herwijnen, Ledertechnologie, 's Hertogenboch, 1956.
4. W. Hausam, Die bacteriologie in der Lederindustrie.
5. J. Wilson, Modern practice in leather manufacture.
6. G. McLaughlin and E. Theis, The chemistry of leather manufacture.

ABSTRACT

Shrinkage temperature (T_s) measurements of collagen hydrothermal stability provide information on the deterioration of skin and semi-tanned leather, on temporary and irreversible effects of conservation treatments and on the effects of storage and display environments. Microscopical methods for measuring the T_s require only minute samples of collagen fibers. This permits the use of such methods for characterizing and monitoring museum artifacts. Basic equipment requirements include a controllable heating element and the means with which to examine fibers at 5 to 100 times magnification as they are heated. A polarizing microscope with hot stage is recommended to achieve high precision in the measurements. Preliminary results support a broad usage of the technique. Shrinkage temperature values for archaeological and ethnographic artifacts occur over a greater than 30°C range below normal values, indicating that varying amounts of deterioration are distinguishable. A lowered T_s for fibers in the presence of some conservation materials that swell collagen reversibly indicates molecular and fibrillar destabilization which could raise the potential for deterioration.

Keywords: COLLAGEN; SKIN; SEMI-TANNED LEATHER; HYDROTHERMAL STABILITY; SHRINKAGE TEMPERATURE; DETERIORATION; TREATMENT MONITORING; MICROSCOPY

MICROSCOPICAL HYDROTHERMAL STABILITY MEASUREMENTS OF SKIN AND SEMI-TANNED LEATHER

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1.0 Introduction

The quantity and importance of skin and semi-tanned leather artifacts in museums warrant greater efforts to develop improved methods of treatment and preservation. Analytical methods are needed to drive such development, and they are needed in practice to give conservators information about the state of artifacts for use in formulating treatments. Analytical methods are needed for-- 1) assessing deterioration, 2) evaluating the effects of established and experimental conservation treatments and 3) monitoring the condition of collections in museum storage and display.

One obstacle restricting analysis of artifacts is the sample size requirement. Several analytical methods are available, but most require comparatively large amounts of material (1). Only microanalytical techniques that require minuscule samples are appropriate for characterizing artifacts and for investigating the effects of treatments on artifacts.

The following paper discusses one such technique which, by assessing the hydrothermal stability of collagen fibers, has the potential for satisfying some of the current analytical needs for skins and semi-tanned leathers. Hydrothermal stability is determined, in part, by measuring the temperature at which collagenous materials shrink in water or in specific aqueous media (2). A microscopical method (3) discussed here requires only minute samples of fibers to measure such temperatures. Preliminary results from surveys of ethnographic and archaeological artifacts are presented to illustrate the broad range of deterioration measurable by this method. Other evidence illustrates that environment and some materials used in treatments can affect collagen fiber hydrothermal stability.

2.0 Collagen Structure and Hydrothermal Stability

Skin and leather artifacts are composed of bundles of collagen fibers. Fibers are composed mostly of fibrils and these, in turn, of collagen molecules with some covalently bound carbohydrate (the collagen monomer formerly called tropocollagen). Several types of collagen exist, and the one designated "type I" predominates in mammalian skin and hide. The collagen molecule consists of three peptides which twist axially about each other for most of their lengths to form a triple helix approximately 280 nm long by about 1.5 nm in diameter. The amino acids glycine, proline and hydroxyproline play major roles in the assembly and rigidity (semi-flexible in solution) of the helix, and hydroxyproline is particularly important for helical stability. The position of polar and nonpolar amino acid side groups on the peptide chains causes the molecules to assemble side-by-side in a staggered manner. This produces fibrils with a periodic (approximately every 67 nm) banding which can be seen in electron micrographs of negative-stained collagen (4). Fibrils range in diameter from 16 nm up to about 1500 nm for all types of collagen, and, as is the case for fibers, fibrillar length is indeterminate.

Hydrothermal stability is mostly a function of the hydrogen bonding between peptides in the collagen molecule triple helix, but an important additional contribution to stability comes from molecular packing and tissue structure in fibrils and fibers (5). Other bonding, *i.e.* molecular and fibrillar covalent cross-linking, determines, in part, such properties as swelling and solubility potential (6) and tensile strength at the fibril level.

Collagen molecules exist in fibrils in a highly organized, partly crystalline state. When subjected to temperatures which melt, *i.e.* denature, this protein (7), collagen fibers lose this organization which cause them to shrink to about one-third of their original length. Hydrothermal stability decreases as a result of a decrease in crystallinity and a loss of molecular order in amorphous areas, both through swelling and deterioration. This is reflected in the shrinkage of fibers in water at temperatures below normal ranges, *e.g.* 62° to 68° C for untanned mammalian collagen. (Shrinkage of extremely deteriorated collagen fibers in water can occur even at room temperature.)

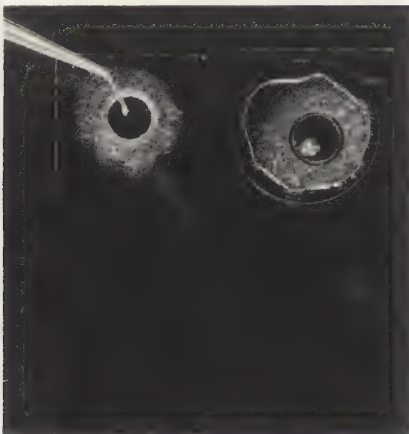


Figure 1. Placement of a sample of water-soaked fibers into the reservoir of a modified glass slide (left); sample contained in reservoir under coverslip (right).



Figure 2. Next page for 2d - 2f.

Deterioration lowers the shrinkage temperature (T_s), whereas tanning raises it by introducing additional cross-linking, thereby reducing the ability of the collagen to hydrate (7). Typical values for vegetable-tanned leather range from the mid 70's to the mid 80's ($^{\circ}\text{C}$). Chrome tanning raises the T_s to over 100 $^{\circ}\text{C}$. Formaldehyde tannage raises the T_s to the low 80's, and oil and smoke tannage change the T_s very little.

3.0 Microscopic Methods of Measuring Shrinkage Temperatures

Since before 1900 a simple "boil test" has been of practical use in the production of chrome-tanned leather to determine the degree or completeness of "leathering" in the manufacturing process. Essentially, if a sample of a chrome leather does not curl within the first few minutes of being placed into boiling water, tanning is complete. Research into the use of shrinkage temperature (T_s) measurements to determine degree-of-tannage began soon after the turn of the century (8). Borasky and Nutting (9) introduced the microscopical method for measuring T_s . With it, they examined the effects on T_s of tannage, stratigraphy and selected peptizing electrolytes.

The microscopical method has several advantages over the standard techniques which require that strips of skin or leather be immersed in a heated bath of water or in a glycerin/water mixture (9). In conservation, the outstanding advantage of the microscopical method is that only minute samples of collagen fibers are required when carrying out the measurements. Individual dry samples taken from artifacts are only .1 to .5 mg. (When wet, a sample is about double the size of a typewritten period.)

3.1 Apparatus

The equipment needed to measure T_s microscopically includes a controllable and measurable heating element and a way to examine collagen fibers visually at a magnification of between 5 and 100 times as they are heated. A melting point apparatus can be used which includes a simple optical magnifier and contains fiber samples in water inside sealed capillary tubes or some other support vehicle. Even a hot plate with fibers contained between a microscopical glass slide and coverslip could be used, along with a hand held magnifying glass to see the fibers. As for any method however, one must be able to-- 1) measure precisely the temperature of the heating element, 2) calibrate temperature against substances with known melting points to determine the accuracy of the measurements, and 3) control the rate of heating. Where thermal analytical techniques are unavailable, a polarizing microscope fitted with a microscopical hot stage is best used. The choice of apparatus will depend on the needed level of precision and accuracy in the measurements and, of course, on the availability and cost of the equipment.

Precision requirements depend on the use to which the information inferred from T_s measurements is put. For example, a decision for or against the use of aqueous treatments might be required for a specific artifact. Even low precision ($\pm 4^{\circ}\text{C}$) could be acceptable for this. Shrinkage in the low 40's ($^{\circ}\text{C}$) or lower would indicate against aqueous treatments because of the possibility of denaturation occurring during conservation. On the other hand, with shrinkage in the high 40's or higher, aqueous treatments might be safely used.

Other circumstances will require higher precision. For example, museum display conditions, such as continuous high levels of lighting during opening hours, will warrant monitoring for even small changes in the hydrothermal stability of artifacts--particularly those made of supple, native-tanned hide. A high degree of precision ($\pm 1^{\circ}\text{C}$) is necessary to ensure that any small measured change that occurs over a short time period (e.g. a month or a year) actually reflects a real change in the artifact. (Evidence of deterioration would encourage changes to display and storage conditions to improve preservation.)

Both the melting point apparatus and hot plate techniques suffer from a lack of precision, particularly because of difficulties with visually detecting the beginning of fiber shrinkage. Both may also suffer from slow sample preparation and slow cycling back to the starting temperature between measurements. The hot plate technique has the added disadvantage that the fibers can be physically prevented from shrinking until higher temperatures are reached because of being sandwiched, and thus restrained, between slide and coverslip. This obviously reduces accuracy.

The polarizing microscope/hot stage combination has the advantage of speed (up to 30 or more measurements in a seven hour period), greater precision and accuracy (particularly if temperature is computer controlled), and ease of use. This is accomplished partly because a polarizing microscope makes the detection of shrinkage



Figure 2 (continued). Portion of fiber sample in polarizing microscope (slightly uncrossed polarizers) showing shrinkage and loss of birefringence (brightness) during heating. Fibers before shrinkage, 2a; nearly complete shrinkage, 2f.

easier. Crossed or slightly uncrossed polarizers enhance detection by revealing the loss of birefringence (brightness) of the fibers as they shrink. This gives greater precision to the measurements by permitting a more exact definition of the shrinkage process.

4.0 Working Definition for Shrinkage Temperature Measurements by Polarized Light Microscopy

A working definition of the shrinkage temperature range, given in terms of phenomena observable in a magnified image of collagen fibers, must be established in order to achieve the best possible precision among measurements. For the preliminary results described below, the shrinkage range is defined at the high end by the temperature corresponding to the loss of approximately 90% of the birefringence of the fibers in the polarizing microscope/hot stage. This corresponds to 90% of total possible shrinkage.

The lower end of the range, the onset of shrinkage, is more difficult to define, because some fibers begin moving and shrinking three or more degrees below the temperature at which other fibers begin. Moreover, shrinkage, even of individual fibers, can have a rather slow beginning. For the present work, therefore, the onset of shrinkage was defined by the temperature at which the loss of birefringence is visible on parts of roughly half of all individual fibers in the sample.

5.0 Method for Assessing Deterioration

To conduct shrinkage temperature measurements, samples are commonly immersed in water or in an aqueous mixture such as glycerin/water. The collagen fibers are therefore in a swollen state at the time of testing. Swelling forces act on collagen until an equilibrium is reached with the internal forces which maintain the integrity of molecular and fibrillar structure. Hydrothermal stability is dependent on the degree of hydration of collagen, and, therefore, a concomitant change in the shrinkage temperature occurs until swelling is completed. The shrinkage temperature is then a function of the remaining integrity of the collagen structure. Any net positive or negative difference in the T_s value between new, undeteriorated fibers and fibers sampled from artifacts is interpreted as a measure of more or fewer stabilizing forces in the fibers of the artifacts.

Samples (.1 to .5 mg) are taken from different locations on an artifact with the objective that the T_s measurements reflect the full range of deterioration. If only one or two are possible, samples should represent the worst deterioration. Both interior and surface samplings of a skin or semi-tanned leather might be included for comparison.

Samples are degreased in acetone and then placed directly, without drying, into distilled water for 10 to 30 minutes to ensure thorough hydration. In the microscopical experiments reported here, degreased, wet samples were transferred into the small reservoir of a specially modified microscopical glass slide designed to prevent physical restraint of fiber shrinkage, Figure 1. (The reservoir was formed by adhering a portion of a Pasteur pipette, on end, to a slide using a rapidly curing epoxy. After the epoxy cured, the portion of pipette was ground down to a glass ring. This formed a reservoir about 6 mm in diameter and about .5 mm high.) After placing the sample into the reservoir, the latter was filled with distilled water, and a coverslip was applied, taking care that air bubbles were excluded. Mineral oil was placed under the coverslip to surround and enclose the reservoir to ensure minimal evaporation of the water during heating. The slide containing the sample was placed into the hot stage, and while the fibers were under examination in the polarizing microscope, heat was added to give a heating rate of 3° C/min.

A rate of 2° C/min is part of the standard conditions advocated by the British Leather Confederation to measure shrinkage temperatures. Calorimetric study in biochemical research requires rates of 1 K (kelvin) or less. For practical purposes, little difference in values of T_s occurs for rates between 1° and approximately 4° C/min. Above this range the value of T_s rises and averages 3° or 4° higher when measurements are performed at 10°C/min; such higher values are unconventional. For the present experiments, a rate of 3° C/min was used which permitted faster testing without unduly sacrificing conventional accuracy.

When possible, the starting temperature of a measurement should be at least 10° C below the anticipated shrinkage temperature. Therefore, the measurement of the first sample from an artifact with unknown deterioration should begin at room temperature. If extreme deterioration is suspected, a dry sample of fibers taken directly from the artifact should be observed in the microscope while a drop of water is added to see if shrinkage occurs at room temperature.

6.0 Observation of Shrinkage

The view in a polarizing microscope of the shrinkage process is shown in Figure 2. Figure 2a contains collagen fibers in their native, undenatured state. Figure 2f contains the same fibers after shrinkage (denaturation). The loss of birefringence (brightness) of the fibers, as seen with crossed polarizers, occurs simultaneously with shrinkage and, as mentioned, results from the loss of both the crystalline and non-crystalline organization of the fibrils and collagen molecules.

7.0 Potential Uses of Shrinkage Temperature Measurements

7.1 Survey of artifact deterioration

Using the working definition of shrinkage described above, a survey of archaeological and ethnographic artifacts of skins and leathers was conducted to determine the range of values occurring for such artifacts, Figure 3. In addition to having lower onset values of T_s , indicating various levels of deterioration, archaeological and ethnographic samples often have a broader shrinkage range compared to samples of new fibers. This may be explained as follows.

At the level of individual fibrils, some regions are apparently less hydrothermally stable than others because of perturbation or deterioration of crystalline and ordered amorphous structure. The less stable regions begin shrinking at lower temperatures, whereas the more stable regions still denature at higher temperatures approaching more normal T_s values. A similar description applies for fibers. The total of fibril deterioration in each fiber is variable, and, therefore, some fibers begin shrinking at lower temperatures than do others. As a result, the shrinkage range of deteriorated samples can be broad, e.g. 10° or 15°+ C, in addition to being depressed below normal values. Alternatively, more uniform deterioration will result in a narrower range of 5° to 10° C, but, again, the range will be significantly below values for undeteriorated collagen.

7.2 Monitoring of storage and display environments

Added deterioration of an object over time in storage or display can be monitored by use of T_s measurements. This is suggested from measurements of brain-tanned and smoke-tanned hide pieces taken from an accelerated fading study conducted by Miles (10), Figure 4. With exposure to the experimental lighting, the hydrothermal stability of the surface fibers dropped initially very rapidly and continued to drop over the duration of the experiment.

7.3 Analysis and the design of treatments

When the extent and pattern of deterioration of an artifact are known, treatments can be designed to circumvent problems with anticipated responses of the artifact. As an example, analysis before treatment of a waterlogged parchment document (11) included separate T_s measurements of two delaminating strata. One, a very thin layer (<1mm), supported the writing of the document, and the other constituted the remaining thickness. The thin writing support had a lower T_s range compared to the remaining thickness. Based in part on this difference, the two layers were expected to react differently to drying stresses. Treatment was designed to give the best possible contact between the layers during drying to ensure similar amounts of area shrinkage and self-adhesion after treatment.

Often with ethnographic skins and semi-tanned leathers neither physical appearance nor feel gives any indication of the extent of deterioration. Routine measuring of T_s as part of pre-treatment assessments can identify those artifacts which are severely deteriorated, as evidenced by T_s values that are close to, or even at, room temperature. As suggested earlier, such artifacts are susceptible to undergoing irreversible denaturation in the presence of water, as from aqueous adhesives. Under these circumstances, even high moisture contents, as from humidification in attempts to soften and reshape an artifact, can be dangerous.

Collagen hydrothermal stability is reduced by extremes of pH, Figure 5, but it can be similarly affected by certain materials at neutral pH, including some materials that are used in conservation. If no deterioration has occurred, the destabilization is reversible by reestablishing a near neutral or slightly acidic environment and by removing any destabilizing substances. Measurements conducted to determine the effect of conservation materials are carried out not in water but in the presence of the material in the medium or solution used to treat artifacts. There are two potential uses. Materials used on skins and leathers can be categorized into those which destabilize

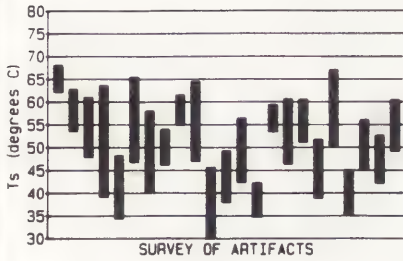


Figure 3. Shrinkage temperature (T_s) survey of ethnographic and archaeological artifacts illustrating the diversity of values. Each bar represents the T_s range from onset (lower limit) to completion (upper limit).

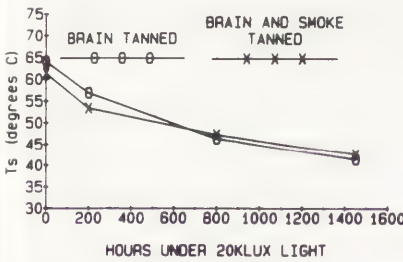


Figure 4. Loss of hydrothermal stability (onset T_s values) in fibers of brain-tanned and smoke-tanned skins subjected to photodegradation by high intensity light.

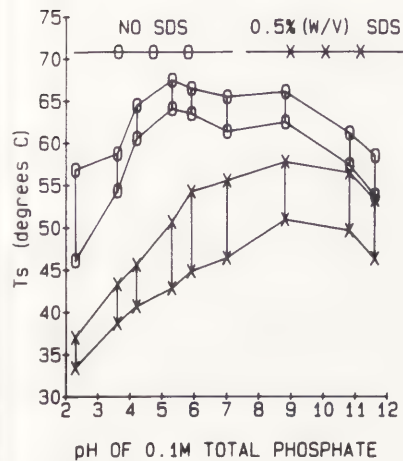


Figure 5. Effect of pH on shrinkage temperature ranges for samples of excavated seal skin. Extremes of pH cause a drastic lowering of the T_s range. Addition of sodium dodecyl sulphate lowers T_s throughout the pH range and causes very low values in acid pH.

collagen structure (even temporarily) and those which do not. For long-term preservation of artifacts, the latter may be preferred. Secondly, proposed treatments can be tested on fiber samples, and thus the actual artifact is not endangered by unexpected treatment effects.

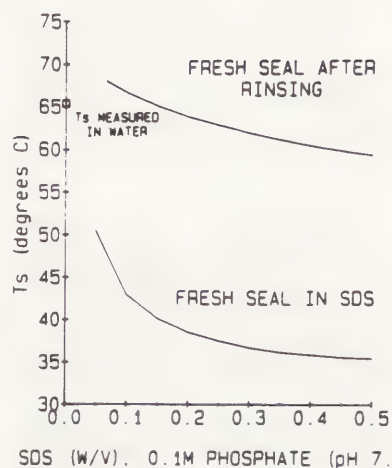


Figure 6. Effect of sodium dodecyl sulphate (SDS) concentration on onset shrinkage temperatures of fresh seal skin. T_s returns almost to normal after rinsing away the indicated concentrations. Very low residues of SDS after rinsing result in slightly higher T_s values compared to those measured in water in the absence of SDS.

The example in Figure 5 is of the effect of the anionic detergent sodium dodecyl (lauryl) sulphate (SDS) on archaeological seal skin taken from Thule excavations in the Canadian high arctic. Destabilization is significant even through the neutral range of pH. Unlike deterioration and photodegradation described above, the effect of SDS on T_s is mostly temporary if exposure is short, as in typical washing treatments. However, irreversible shrinkage of particularly deteriorated portions of experimental samples has been observed under normal treatment conditions.

Most, but not all, of the lost stability is recovered when the detergent is washed from collagen, as revealed in Figure 6. Residual amounts of SDS remain after washing and cause a small but measurable permanent drop in stability. It is noteworthy that exceedingly small residues of SDS actually cause an increase in T_s , but such an effect occurs when SDS has been used at concentrations below the critical micelle concentration, *i.e.* at concentrations which are of little use for cleaning archaeological artifacts.

8.0 Conclusions

The hydrothermal stability of skin and semi-tanned leather artifacts reflect the physical and chemical integrity of collagenous components. Values of shrinkage temperature (T_s) below the normal range of 62° to 68° C in water are consistent with deterioration in artifacts. A drop in T_s indicates disruption of fibrillar crystallinity and of amorphous fibrillar and molecular orderliness, as suggested in cases of extreme deterioration by the association of low T_s values with reduced birefringence observed by polarized light microscopy. Shrinkage temperatures that differ from expected values when test fibers are in the presence of selected conservation materials are consistent with changes in stability. Further research is required for a more complete definition of T_s in terms of artifact deterioration and conservation.

In conservation and research, a potential exists for exploiting hydrothermal stability in - 1) characterizing artifact deterioration, 2) monitoring changes in the stability of artifacts in long-term storage and display, and 3) studying the effects of conservation processes and materials on artifacts. The long-term destructive effects of acidic conditions are well known, particularly for vegetable-tanned leather (*i.e.* red rot), but the effects of potentially adverse conservation materials have yet to be examined. The question of whether destabilized collagenous artifacts are more likely to deteriorate, and therefore degrade more rapidly in storage or display, deserves investigation.

9.0 Acknowledgements

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10.0 Bibliography

1. VAN SOEST, H.A.B., T. STAMBOLOV AND P.B. HALLEBEEK, "Conservation of Leather," *Studies in Conservation* 29, no. 1 (1984): 21-31.
2. HAINES, B.M., "Shrinkage Temperature in Collagen Fibres," *Leather Conservation News* 3 no. 2 (1987): 1-5.
3. YOUNG, G.S., "The Potential of Shrinkage Temperature Measurements in Skin and Leather Conservation," *Ethnographic Conservation Newsletter of The Working Group on Ethnographic Materials of The ICOM Committee for Conservation*, 3 (1987): 16-17.
4. PIEZ, K.A., "Molecular and Aggregate Structures of the Collagens," in *Extracellular Matrix Biochemistry*, eds. Karl A. Piez and A.H. Reddi (Amsterdam: Elsevier Science Publishing Company Inc., 1984) 1-40.
5. KUHN, K., "The Classical Collagens: Types I, II, and III", in *Structure and Function of Collagen Types*, R. Mayne and R.E. Burgeson (Eds.), London: Academic Press, (1987) pp. 1-42.

6. TANZER, M.L., "Cross-Linking of Collagen," Science **180** no. 4086 (1973): 561-566.
7. FLORY, P.J. AND R.R. GARRETT, "Phase Transitions in Collagen and Gelatin Systems," Journal of the American Chemical Society **80** (1958): 4836-4845.
8. NAYUDAMMA, Y., "Shrinkage Phenomena," in The Chemistry and Technology of Leather, vol II, eds. F. O'Flaherty, W.T. Roddy and R.M. Lollar, Tanner's Council Laboratory, University of Cincinnati (New York: Robert E. Krieger Publishing Company, 1978) 28-65.
9. BORASKY R. AND G.C. NUTTING, "Microscopic Method for Determining Shrinkage Temperatures of Collagen and Leather," Journal of the American Leather Chemists Association **44** (1949): 830-841.
10. MILES, C., "Interim Report: Light-induced Colour Changes in Organic Materials," (Conservation Research Services Project #33) Ottawa: Canadian Conservation Institute (1985) (unpublished report).
11. LOGAN, J.A. AND G.S. YOUNG, "A Message in a Bottle: The Conservation of a Waterlogged Parchment Document," Journal of the International Institute for Conservation--Canadian Group **12** (1987): 28-36.



Working Group 19

Easel Paintings on Rigid Support

Peintures de chevalet sur supports rigides



RESUME

Les portraits à l'aquarelle et à la gouache sur ivoire étaient très répandus au XVIIIème et XIXème siècles. La restauration de miniatures trouve sa difficulté majeure dans la fragilité du support: l'épaisseur des plaques d'ivoire est normalement inférieure à 0.5mm. De plus ces matières sont très sensibles aux variations climatiques. Les fissures ou cassures entières sont à traiter en collant des bandes de papier japon au revers avec de la colle animale. Pour l'ajustement délicat des pièces détachées il a fallu élaborer une petite presse transparente en Plexiglas. Le réglage se fait à l'aide de boulons et de languettes en laiton, l'ensemble étant tenu par un serre-joint. Cette construction spéciale peut être changée selon les formats des miniatures, tant pour les portraits ovales que rectangulaires.

MOTS-CLES

IVOIRE, MINIATURE, CASSURE, CONSTRUCTION EN PLEXIGLAS, COLLE ANIMALE

RESTAURATION DE MINIATURES: LE COLLAGE DES SUPPORTS EN IVOIRE A L'AIDE D'UNE CONSTRUCTION APPROPRIÉE EN PLEXIGLAS

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Introduction

Par définition les miniatures sont des objets peints de petites dimensions. Peindre avec beaucoup de finesse se prêtait essentiellement aux techniques d'aquarelle et de gouache sur velin, ivoire ou papier. On peignait aussi de petits portraits à l'huile sur du bois ou du cuivre, et on réalisait des miniatures en émail.

Ici seront traités uniquement les portraits sur ivoire, technique qui se développe au cours du XVIIIème siècle et qui connaît son apogée de la fin du XVIIIème jusqu'au milieu de XIXème siècle.

L'étude suivante est le fruit de plusieurs années de travaux concernant les miniatures sur ivoire. D'anciens traités de peinture de miniatures nous précisent comment le peintre a préparé sa fine plaque d'ivoire afin de peindre dessus (1). Les principales causes d'altérations de miniatures ont pu être étudiées en examinant une grande partie des 270 miniatures conservées dans la "Graphischen Sammlung Albertina", collection d'importance internationale d'oeuvres graphiques à Vienne (2). Les travaux de restauration proprement dits s'étendent évidemment sur un traitement global, depuis le démontage du cadre (fig. 1) jusqu'au réencadrement après la restauration. L'étape la plus compliquée est le traitement du support: l'ivoire peut être altéré par des déformations, des cartons collés au revers, des fissures, voire des fentes entières (fig. 2).

Historique de l'utilisation du support ivoire

Au cours du XVIIIème siècle l'ivoire remplace petit à petit le velin, l'ancien support traditionnel pour les miniatures exécutées à la gouache. Les premières plaques débitées dans le sens de la longueur de la défense d'éléphant ont environ 1mm d'épaisseur et sont opaques. Ceux-ci posent rarement des problèmes de conservation. Au milieu du siècle on découvre que des plaques plus minces (de 0,3 à 0,5mm) permettent de jouer sur la transparence de l'ivoire: une luminosité vivante peut être obtenue dans les visages, parties qui sont peintes par glacis à l'aquarelle en peignant au revers ou bien en plaçant derrière la miniature une feuille d'argent. Afin d'agrandir les formats, on incruste même des pièces d'ivoire dans du carton à l'emplacement des visages, et, vers 1830, on trouve une méthode de découper de plus grandes plaques dans la défense suivant la circonférence (3).

1. bordure du couvercle de la boîte
2. papier avec une esquisse préparatoire de l'épaule, restes d'adhésif (flèche) provenant du collage au dos de la miniature, restes de baudruche (flèche)
3. portrait de jeune femme, aquarelle et gouache sur ivoire, diamètre 63mm
4. verre bombé avec restes de baudruche (flèche) ayant été collée le long du bord du verre et du papier (2) au revers
5. cadre métallique, à l'origine enfoncé dans la couvercle



Fig. 1. Ouverture du montage original d'une miniature décorant le couvercle d'une petite boîte (autrichien, début du 19ème s.).

Préparation des plaques d'ivoire

Quelques altérations de ces fragiles supports trouvent leur origine dans certaines manipulations faites par l'artiste lui-même. Les détails techniques décrits ci-dessous aideront le restaurateur à interpréter et à traiter les dégâts.

Après le contrôle de qualité de la plaque d'ivoire, qui doit être lisse, uniforme et sans irrégularités à l'emplacement du visage, il faut éliminer les rayures produites par la scie en râclant la surface au moyen d'un rasoir ou d'un grattoir. Puis on ponce soigneusement avec de la poudre de pierre ponce.

La découpe des formes ovales se fait à la scie fine, ou bien, dans le cas des plaques très minces, aux ciseaux, en ayant soin de toujours diriger leurs pointes dans l'axe de l'ivoire, sinon il risque de se fendre entièrement. Il est même indiqué qu'il faut tremper la plaque pendant une heure dans de l'eau ou une solution d'alun pour la ramollir avant la découpe. Il va de soi qu'après de tels traitements l'ivoire flexible au départ peut devenir très cassant en vieillissant.

L'ivoire étant très sensible à l'humidité, il a tendance à se gondoler lors de l'application des couches d'aquarelle. Les artistes pensaient y remédier en le renforçant par différents papiers ou cartons (fig. 1), et même par leur propres dessins préparatoires. Voici la description d'un professeur de peinture: "Le collage de l'ivoire offre trop de difficultés pour que je le passe sous silence. Quand la plaque est de petite dimension, voici comment je procède. Après avoir, sur une feuille de carton bien blanc, marqué d'un trait au crayon le contour de l'ivoire, je prends avec un pinceau hors d'usage de la gomme arabique liquide très pure et j'en couvre légèrement le carton en ayant soin de ne pas dépasser le tracé au crayon; puis, avec rapidité, je pose l'ivoire exactement sur la partie gommée et je place le tout entre les feuillets d'un livre que je mets immédiatement sous presse avant que l'humidité de la gomme ait fait gondoler l'ivoire" (5). Pour les formats plus grands que 12 cm il est conseillé d'en coller uniquement les bords ou les quatre coins. Tels cartons plus ou moins bien collés poseront différents problèmes de conservation.

La surface ainsi préparée reçoit une très légère esquisse au pinceau, qui souvent peut être décalquée d'un dessin préparatoire posé au dessous de l'ivoire. Après une ébauche aux larges coups de pinceau, si l'on peut dire, l'artiste superpose en pointillant ou hachurant des couches de couleur pour la finition du portrait. L'exécution à l'aquarelle permet d'avoir un maximum de légèreté dans les visages. Selon les écoles, les fonds et draperies peuvent être exécutés à la gouache. On peut rendre la couche picturale plus brillante et les ombres plus profondes en délayant les couleurs avec de la gomme arabique dissoute dans l'eau, avec une adjonction de sucre candi ou de glycérine en guise de plastifiant.

Fig. 4. Face de la miniature après collage de la fissure. Grâce à l'ajustement précis on a pu éviter toute retouche.

Fig. 5. Revers de la miniature, le collage d'une bande de papier japon à l'aide de la colle animale permet de voir la transparence de la matière.



Fig. 2. Portrait anglais du début du 19ème siècle, aquarelle sur ivoire, 73 x 59mm. La miniature présente une large fissure causée par un encadrement trop serré.



Altération des supports en ivoire

Les plaques plus épaisses posent peu de problèmes par rapport à celles qui sont très fines. Au moindre changement d'humidité relative ces dernières ont tendance à se gondoler, et il suffit qu'une miniature sans cadre soit exposée pendant 10 minutes aux rayons du soleil pour qu'elle se courbe parallèlement à la veine de l'ivoire de manière concave. Souvent le carton de renforcement cause des déformations partielles aux endroits où les points de colle sont appliqués irrégulièrement. Ceci s'explique par la nature hygroscopique de l'ivoire et sa tendance à rétrécir sa largeur lors du vieillissement (6). Si les tensions causées par les matériaux secondaires utilisés sont trop fortes, l'ivoire se fissure ou se fend entièrement. Des cassures accompagnées de part et d'autre de cuvettes peuvent être causées par un encadrement trop serré (fig. 2). La plupart du temps, le verre bombé, la miniature, et le revers en carton sont à l'origine assemblés en collant le long des bords une bande de papier, ou de baudruche (fig. 1). Le microclimat enfermant la miniature peut causer des condensations, ou des dépôts cristallins sur le verre (7). Il ne faut pas oublier l'utilisation des miniatures aux siècles derniers comme bijoux, médaillons ou "objets de coeur" portés avec soi dans un étui de cuir. L'ivoire découpé selon la circonférence de la défense aura tendance à reprendre sa forme initiale courbée. Pires sont les altérations des grandes miniatures formées par plusieurs pièces d'ivoire, parfois rapiécées à contre-fil: les fentes causées par le dessèchement sont très larges.

Traitement des déformations des plaques d'ivoire

Avant de pouvoir ajuster les ivoires fendus, il faut traiter les déformations. Les cartons collés aux revers seront coupés couche par couche à sec, les restes de colle et de carton seront ensuite enlevés avec la moindre quantité possible d'humidité (par exemple avec une solution inférieure à 50% d'eau dans de l'alcool). L'ivoire libéré peut parfois retrouver une forme plane après quelques jours. Dans le cas contraire il faut le presser, entre des plaques de Plexiglas de préférence, en augmentant au fur et à mesure la force appliquée. Pour les ivoires très cassants un traitement préalable du revers par cette solution d'eau dans l'alcool ou par un mélange d'alcool, d'acide acétique et d'huile d'amandes facilite cette tâche (8). Souvent il faut laisser la miniature 1 ou 2 mois sous presse.

Construction d'une "presse spéciale pour miniatures" en Plexiglas

La première "presse pour miniatures" réalisée totalement en Plexiglas et montée par collage des pièces a été fabriquée sur mesure pour une seule miniature en 1983 (fig. 6).

- 1. plaque en Plexiglas de base
- 2. plaque fixe collée sur la plaque de base, découpée selon la forme ovale de la miniature
- 3. pièces biseautées permettant aux morceaux mobiles de coulisser, collés sur la base
- 4. écrous collés sur la base
- 5. plaque mobile resserrant la cassure
- 6. couvercle en Plexiglas, un peu plus petit que la miniature

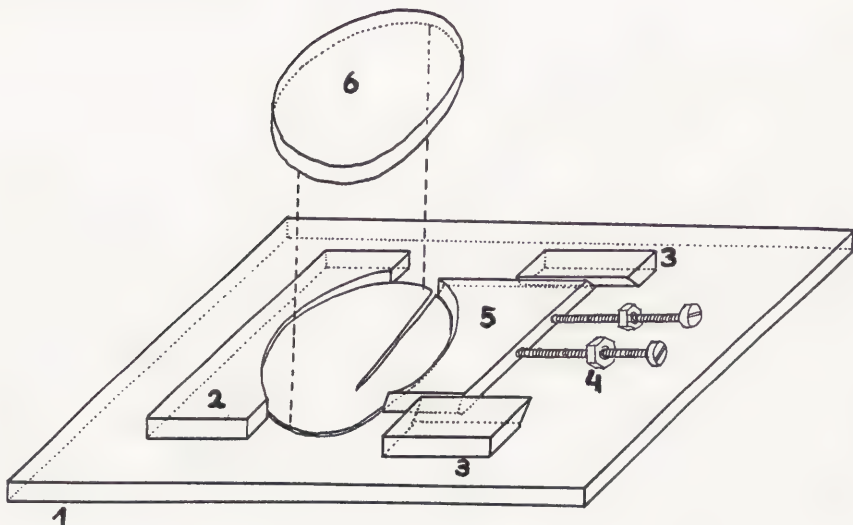


Fig. 6. Presse de Miniature en Plexiglas n°1 fabriquée sur mesure pour un portrait ovale.

La restauration de plusieurs miniatures incitait à élaborer un autre modèle (fig. 3,7) adaptable à différentes grandeurs: les pièces réutilisables et devant rester immobiles seront montées à l'aide de boulons et écrous sur une plaque de base trouée aux bords. Il suffit alors de fabriquer sur mesure des languettes en découpant au bœfil des plaques de laiton de 0,3 à 0,5mm d'épaisseur. La presse, une fois installée pour une certaine mesure d'une miniature, s'utilise de la manière suivante:

1. Poser la miniature, (couche picturale vers le bas) sur la plaque de base.
2. Mise en place de la plaque de laiton (n°3) qui restera immobile.
3. Mise en place des languettes en laiton et des poussoirs de Plexiglas (n°5 a,b) et resserrer légèrement les boulons (n°4), sans forcer la miniature. Dans des cas compliqués, on attache provisoirement l'ivoire à l'aide d'un petit bout de ruban adhésif à la languette.
4. Pose du couvercle (n°6) et du serre-joint, resserrer très légèrement.
5. Ajustement en fermant progressivement les boulons. Les fissures à grand écart ne se referment qu'en répétant ce traitement pendant plusieurs jours (fig. 8).
6. Resserrement du serre-joint.

Si la couche picturale présente de légers empâtements (au niveau des rehauts, perles, etc), on peut insérer entre la peinture et le Plexiglas des feuilles de melinex ou de nylon.

Fig. 3. La miniature précédente ajustée dans la presse en Plexiglas n°2. La photo montre la construction vue du bas, c.à.d. à travers la plaque de base (n°1 de la fig. 7.).

1. plaque de base en Plexiglas (épaisseur 8mm) avec tout autour deux rangées de trous (distants de 15mm) permettant différentes positions des barres de laiton n°2 et 4
2. barre en laiton fixée et écrous bloquant les plaques de laiton n°3
3. plaque en laiton (0,3-0,5mm d'épaisseur) fabriquée sur mesure pour chaque miniature
4. a. barres en laiton avec deux trous pour le montage sur la plaque de base, et un filet percés à l'aide d'un taraud pour les boulons (diamètre 3mm)
4. b. en cas de besoin de beaucoup de boulons ou pour des miniatures rectangulaires, on peut utiliser une longue barre en laiton avec deux trous pour le fixage sur la plaque de base, et plusieurs filets percés pour les boulons
5. Languettes mobiles en laiton fabriquées sur mesure (5a) et poussées par des petits poussoirs en Plexiglas (5b)
6. Couvercle en Plexiglas (8mm)

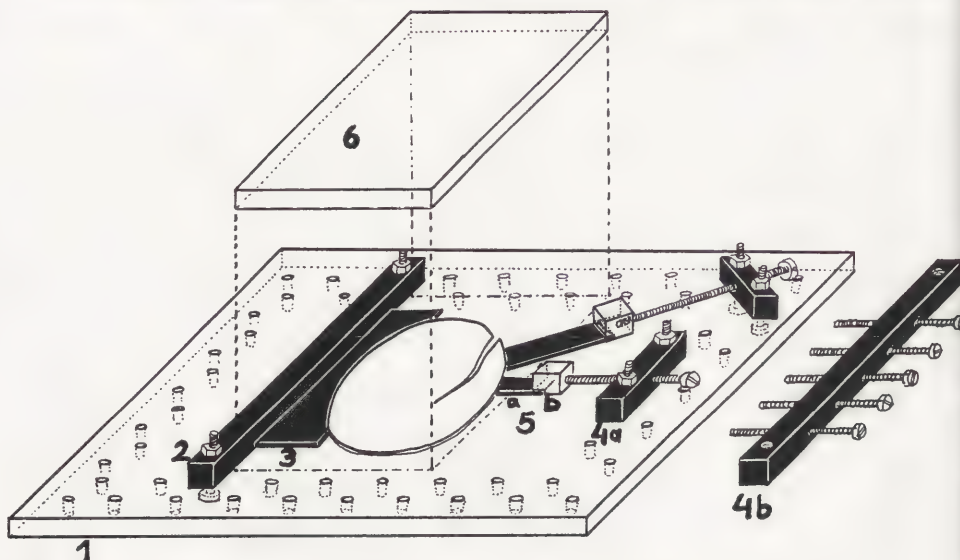
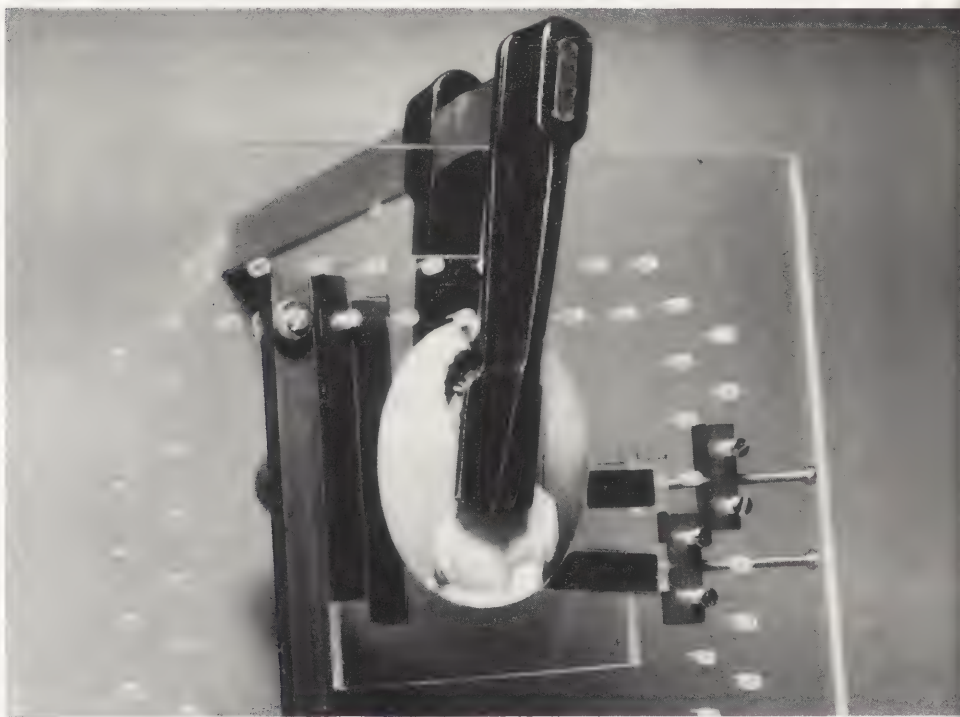


Fig. 7. Presse en Plexiglas n°2 pour des formes et dimensions variables.

Collage des ivoires cassés

L'étape de collage peut commencer si l'on a préalablement traité les déformations et si l'ajustement de la miniature dans la presse est parfaite: il faut laisser s'habituer la miniature à sa nouvelle position pendant quelque temps, de préférence plusieurs semaines. Avant d'enlever le serre-joint on ouvre les boulons pour desserrer les poussoirs en veillant bien à compter le nombre de tours, pour pouvoir lors du collage les resserrer de manière identique. On prépare alors des feuilles de papier silicone (blanc et légèrement transparents) pour le revers et de melinex pour pouvoir observer les manipulations de face. Murrell a proposé d'isoler les bords de la fissure avec une résine acrylique en solution ou de la cire microcristalline. Ceci n'est pas nécessaire si l'ajustement est optimal comme pour les cassures nouvelles. Dans le cas des fentes anciennement collées, il est souvent très difficile, même au microscope binoculaire, de nettoyer l'adhésif restant dans la fissure. Lors du collage il faut, comme déjà signalé, éviter l'utilisation d'une grande quantité d'humidité, même si la miniature ne peut pas bouger dans cette presse. Il est donc conseillé de procéder à un collage partiel en utilisant une bande de papier japon (large de 5 à 8mm, de couleur appropriée et d'épaisseur moyenne, fig. 5). Elle sera appliquée au revers, au niveau de la fissure, à l'aide de la colle animale, adhésif choisi en fonction de son pouvoir collant et de sa composition chimique proche à celle de l'ivoire (9). Il faut choisir une qualité flexible comme la colle de peau de lapin (colle Totin), la préparer de manière assez épaisse et l'appliquer en couche mince à chaud sur le papier japon. On ferme ensuite rapidement la presse, ce qui est difficile pour les cassures compliquées. Dans ces cas on laisse gélifier et légèrement sécher toutes les petites bandes préparées. On les pose aux endroits prévus, puis on réactive l'adhésif à l'aide d'une spatule chauffante. On peut alors vite fermer, placer le serre-joint et resserrer les boulons (fig. 3).

On pourra aussi envisager d'utiliser une colle de peau plastifiée à la thio-urée, utilisable à froid, mélange récemment testé à l'IRPA et obtenant les meilleurs résultats pour le collage des panneaux sur bois (10).

Si l'on ne peut pas éviter un doublage (ou marouflage) complet de la miniature pour des raisons de trop grande fragilité, ou à cause de graves déformations qui réapparaissent, il faut l'effectuer lors d'une seconde étape, où l'on n'aura alors plus besoin de la construction en Plexiglas. On peut choisir la méthode longuement pratiquée au Victoria and Albert Museum, avec de la colle animale sur un support épais fabriqué spécialement par lamination de papiers (11). Si on veut éviter l'humidité, on attachera plutôt la miniature à un carton non acide, en réactivant une couche d'adhésif acrylique appliqué sur le support de renforcement par un solvant approprié (par exemple l'adhésif acrylique Lascaux 498 20X réactivé au toluène).

Conclusion

Un collage des cassures de miniatures sur ivoire au moyen de bandes de papier japon et de colle animale laisse visible un maximum du revers de la miniature (fig. 5). L'ajustement optimal grâce à la presse en Plexiglas permet normalement d'éviter les retouches le long des fissures, ce qui est un grand avantage du point de vue de la restauration. Le succès du collage pourra rendre les fissures dans les parties aquarellées quasiment invisible à l'oeil nu (fig. 4). Les parties à gouache sont toujours plus délicates: même une fente bien resserrée aura l'aspect d'une fissure dans une porcelaine.

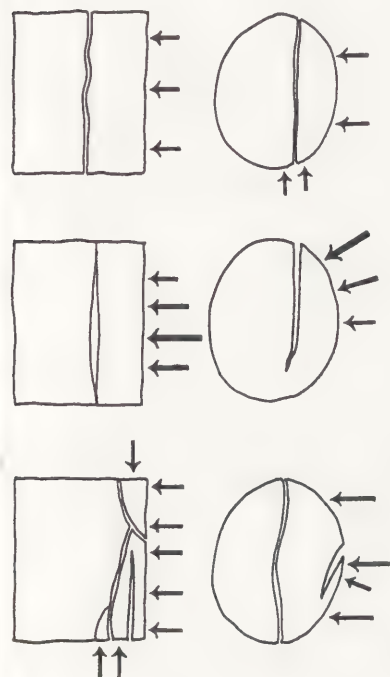
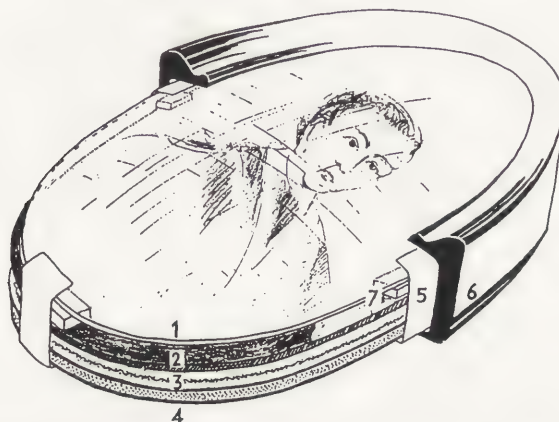


Fig. 8. Exemples de pressions à appliquer selon les différents types de cassures. Dans le cas des miniatures fendues entièrement il faut souvent aussi appliquer des pressions de part et d'autre de la cassure pour assurer une parfaite mise en place des 2 morceaux.

Fig. 9. Conseil de montage d'une miniature dans son cadre:

1. verre bombé
2. miniature sur ivoire
3. soie teintée posée derrière l'ivoire
4. carton protégeant le dos
5. morceau de papier japon collé le long des bords, fixant le verre, la miniature et le carton
6. cadre décoratif
7. taquet en carton inséré entre la miniature et le verre



Il faudra observer pendant quelque temps le comportement de la miniature collée: de légères courbures qui reviennent devront être acceptées. Le montage dans le cadre doit souvent être modifié de manière à laisser un peu de jeu à l'ivoire, et permettre aussi le passage de l'air pour éviter les problèmes de microclimat. Ceci peut être effectué en insérant des taquets de carton non acide entre le verre et la miniature, le tout tenu ensemble par collage aux bords à 4 ou 6 endroits de morceaux de papier japon ou de boudruche (fig. 9).

Notes

- (1) **C. Chizzola**, "Maltechnik und Restaurierung von Portraitminiaturen auf Elfenbein", Restauratorenblätter 8 (1985-86) Hrsg. Österreichische Sektion des IIC, 71-82. Cette étude compare neuf traités de peinture de miniatures datant de 1681 à 1927, décrivant les propriétés de l'ivoire, les procédés de blanchiment, de ponçage, puis la préparation du liant et des couleurs, enfin les différentes manières d'exécuter la peinture.
- (2) **N. Keil**, Die Miniaturen der Albertina in Wien (Wien, A Schroll, 1977).
- (3) **J. Murrell**, "The Restoration of Portrait Miniatures", Conservation and Restoration of Pictorial Art, éd. Brommelle and Smith (London, Butterworths, 1976), 130.
- (4) **G. Banik, C. Chizzola, E. Thobois, J. Weber**, "Formation de dépôts cristallins sur la paroi interne des verres d'encadrement de miniatures sur ivoire", Journées sur la conservation, restauration des biens culturels, (Paris, 2-4 Novembre 1989, éd. Association des restaurateurs d'art et d'archéologie de formation universitaire), 178.
- (5) **G. Debillemont-Chardon**, La Miniature sur Ivoire, Essai Historique et Traité Pratique (Paris, H. Laurens, 1909), 70.
- (6) L'ivoire frais contient 20% d'eau, séché, il en contient 12%. L'article suivant décrit les propriétés physiques et les altérations de l'ivoire en général:
R.H. Lafontaine, P.A. Wood, "The Stabilization of Ivory Against Relative Humidity Fluctuations", Studies in Conservation 27, no. (1982), 109-117. Les altérations des supports ivoire ont été décrits et illustrés par:
J. Murrell, "Structural Defects in British Portrait Miniatures", Preprints for the UKIC 30th Anniversary Conference, (London, 10-14. oct. 1988), 73-75.
C.T. Chieffo, "Painting in Little, Problems in Conserving Portrait Miniatures on Ivory", Preprints for the AIC 10th Annual Meeting, (Milwaukee, Wisconsin, mai 1982), 76.
- (7) **Banik**, "Formation de dépôts", 178, 181.
- (8) **Murrell**, "The Restoration", 131. Au Victoria and Albert Museum a été élaboré le mélange suivant: 1-5% huile d'amandes, 10% acide acétique, 85% alcool à 90°. Dans des cas extrêmes Murrell conseille de râcler le dos de l'ivoire pour éliminer la couche superficielle imperméable, durcie par la colle.
- (9) **R. Weber, H. Kawinsky**, "Restaurierung eines Elfenbeinzinken", Arbeitsblätter des ATM 1 (1984), 41. L'ivoire d'éléphant est composé aux trois quarts de matières inorganiques (phosphates de calcium avec un peu de carbonate de calcium et de fluorure de calcium) et d'un quart de matières organiques (collagène et élastine). La colle forte est actuellement encore utilisée pour coller l'ivoire sur les touches de piano blanches.
- (10) **J.A. Glatigny**, "Evolution des matériaux utilisés à l'IRPA, Bruxelles, à travers un exemple dans le domaine du collage des panneaux", Journées sur la conservation, restauration des biens culturels, (Paris 1989), 45. 1000g de colle de peau de bovin (Holding Trobas B.V. 100 milipoises) + 150g de thio-urée ($\text{NH}_2 \text{CSNH}_2$) + 200g d'eau + 4g de Nipagine. La thio-urée ralentit le temps de prise en gel du mélange, améliore le comportement de la colle et agit comme plastifiant en s'insinuant entre les chaînes de collagène.
- (11) **Murrell**, "The Restoration", 132. "support specially prepared by laminating hot pressed rag paper", ceci pour éviter les tractions selon la direction du papier.

ABSTRACT

The iconostasis of a Serbian Orthodox monastery church in Grábóc includes two oval icons painted on iron plates which required restoration. Chemical and electrochemical treatments were applied: Na-glyconate solution, solvate, thioglycol acid, and local electrolysis. Losses were complemented with fiberglass silk patches reinforced with acrylate-type resin.

KEYWORDS

Icon paint on iron, painting conservation, local electrolysis.

RESTORATION OF TWO ICONS PAINTED ON IRON PLATES IN THE EASTERN ORTHODOX CHURCH IN GRÁBÓC

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Introduction

The iconostasis of the Serbian Orthodox Monastery Church in Grábóc includes two oval icons, "Flight to Egypt" and "Jesus in the Temple at Age Twelve." These two images were painted on iron plates in the nineteenth century to cover over the original canvas paintings that framed the royal door of the church (1).

Iron as a support for paintings

With the development of metal plate manufacture in the mid-eighteenth century, metal became a commonly used support for paintings in eastern Europe, particularly for miniatures, coats-of-arms, and sign boards. It was found that the properties of metals such as copper, zinc, silver, and iron offer these advantages: 1 a thick coat of primer is not required to achieve a smooth surface; 2 metal supports are less vulnerable to expansion and shrinkage caused by heat or moisture than are fibrous materials; 3 they are resistant to insects.

These metals are, however, also subject to liabilities: 1 conspicuous corrosion may gradually destroy the paint layer; 2 like other metals, they can be damaged by pressure or impact; 3 buckling edges may break off or warp, causing the priming and paint layers, which do not adhere well to smooth surfaces, to flake off.

According to the literature, preparation of iron plates for painting proceeds in the following way. First, all traces of rust are thoroughly removed. Then the plate is heated, coated with a thin linseed oil varnish, and allowed to cool. Next, the surface is primed, usually with white lead mixed with linseed varnish, applied in several (usually three) layers of stippling. The surface is then polished with fine pumice flour (2, 3).

Pre-treatment condition of the icons

Plate size (maximum diameters): 58 cm, 92 cm

Original thickness: approximately 0.7 mm

Iron is the metal most susceptible to corrosion. Contact with any amount of moisture causes the surface layer of iron oxide to transform into ferric hydroxide. Iron oxides and ferric hydroxides are commonly called "rust", the main component of which is red iron oxide Fe_2O_3 (hematite). Rust may also contain yellowish brown iron carbonate FeCO_3 (siderite), grayish-yellow iron sulphide FeS_2 (pyrites), as well as compounds with a dangerous chloride content (4).

The humid church atmosphere and surrounding trees have promoted the heavy corrosion of the two icons, which are known to have been positioned at the lower part of the iconostasis, near to the ground.

Plate 1, "Flight to Egypt," may have been exposed to more severe chemical and electrochemical effects than its counterpart. Corrosion across almost the entire width left the icon in a fragile condition (see Fig. 1). Rust had



Fig. 1 Condition of the icon
"Flight to Egypt"
(Plate 1) when taken over



Fig. 2 Condition of the icon "Jesus at 12 Years in the Temple" (Plate 2) when taken over

damaged the plate edges—the lower and upper arcs and right edge. An important part of the lower right arc — approximately 30 sq.cm — was missing: about 3 to 4 cm from that same edge corrosion had completely perforated the metal in a hole of about 8 sq. cm. A white, dusty layer of varying density covered the image along with numerous patches of rust, rendering both the design and colours almost indiscernible.

Certain heavily corroded parts of the plate where there was no paint layer showed friable white spots (possible the priming layer) that were in all likelihood swollen by humidity. Yet, in spite of this damage, the image did not flake off or exhibit a pattern of cracks. The rust, however, had caused the surface to become rough by stretching the priming and paint layers as it expanded.

Plate 2, "Jesus in the Temple at Age Twelve," was in visibly better condition (see Fig. 2). While the surface was rusty, the iron support was strong, elastic, and much thicker than its mate. It was curious to note that this plate also had suffered the most damage to the edge of the lower right arc. In places, the icon surface was veiled by a whitish "gauze," but the rust that had issued from the iron plate caused much less damage. A thick, dirty, grease stain in the center of the icon, probably from an oil lamp, concealed the subjacent details. Wax drops, probably from candles, had burned through the paint down to the iron support in places.

Essential questions

Preliminary tests, empirical observation, and treatment results focused on the following questions:

1. What agents were present in the primer and paint?

Thin-section microscopy tests of the binders of the primer, paint, and stratification were conducted by Klára Török-Erdőhalmi and Márta Bendefy-Kiss. Primer and paint layers of both icons were found to be made with an oil binder without protein.

2.a What is the origin of the off-white coating on the pictures?

No test was made to determine the composition of the coating, though empirical observation indicates that it is a varnish layer partially transformed by severe environmental effects such as temperature variation, high relative humidity, and moisture. Simple mopping with distilled water removed most of the deposits on the varnish surface.

2.b What is the origin of the white "efflorescent" spots on the most damaged parts of icon No. 1, as shown in figure 3?

As mentioned above, these spots were thought to be residues of the priming layer, altered by humidity and corrosion. This conjecture was supported unequivocally by the results of the Debye and Sherrer X-ray diffraction tests carried out on a sample (Cu tube - Ni filter - 60 mA, 40 kV - exp. time 3 hours).

Analysis of the tested material suggests the presence of ZnO and $BaSO_4$, ingredients in lithophone primer, which was invented in 1847 and manufactured for industrial use starting in 1874 (5). These tests and evaluation of the results were carried out by László Kriston (National Institute of Forensics Science) and Márta Járó (National Centre of Museums).

3. Which solvent is suitable for removing the oil stain from the painted surface of plate No. 2?

A 1:1 mixture of ethyl-acetate ($\text{CH}_3\text{-CO-C}_2\text{H}_5$) and methyl-ethyl-ketone ($\text{CH}_3\text{-CO-C}_2\text{H}_5$) seemed indicated. This mix has the solubility parameters $f_D 52$, $f_P 22$, $f_H 26$ (after the Teas and Torraca table) and lies within the solubility regions of proteins, polysaccharides, resins, oils (6), i.e., it was able to dissolve them.

4. How can rust stains be removed without harming the painting (Fig. 3)?

For treating iron objects combined with organic material, Na-glyconate in a neutral (pH 7) rather than in a basic solution proved to be an effective detergent. While this method successfully removed the rust stains, the drawback was that the time required to dissolve the brown colour - approximately 15 minutes - caused some pigments to fix the agent to the extent that after the treatment the subsisting yellow fur could no longer be removed by rinsing with distilled water. This was probably due to the reaction of ferrous pigment materials.

Thus, for treating those surfaces where rust stains enveloped the picture, a more suitable method had to be found. Here Péter Jánoska's experience in the treatment of Avar Age metal finds provided the way (7). Jánoska had successfully applied Sorbiteas as a gentle "rust solvent" to the metals (sorbite, a white powder of a hexavalent alcohol - Glukonon made in the GDR). To a 10% solution of sorbite, CMC was added as a thickening agent; the resulting material was applied to the painted surface. The effect of this treatment was that "lost" details reemerged, and even those rust stains that had penetrated the paint layer disappeared completely. (See Fig. 4.)

5. What is the best solvent for removing the yellowed varnish?

Various tests again showed the 1:1 mixture of methylethyl-ketone to ethyl-acetate to be most effective, while in places a 3:1 mix of benzene to ethanol was used for cleaning with solubility parameters ($f_D 79.5$, $f_P 6.75$, $f_H 13.75$) defining the solubility range of oils and waxes. The dirty lacquer covering the light colours in both paintings was most effectively removed using a 12% soapy ammoniacal spirit. Subsequent mopping with white spirit reduced the effect of solvent remaining in the primer and paint layers.

6. What is the origin of the bluish-black layer that covers almost completely the reverse side of plate No. 2, appearing also in spots on plate No. 1?

Metal experts readily identified this metallic hard layer as magnetite. A linseed varnish applied to a de-rusted iron plate results eventually in a shiny, highly resistant hard iron oxide surface layer (Fe_3O_4 - magnetite) that acts as a type of protective layer in resisting iron corrosion. In the course of cleaning it was revealed that the magnetite layer is continuously present underneath the priming layer. This unusual occurrence will require further study.



Fig. 3 A. Detail of icon No. 1, showing the defects, on the one hand of the white "efflorescence" surrounding the rust that had penetrated the painting; and on the other hand, of rusty spots imbibed in the paint layer
B. The same detail after Sorbite treatment

The cleaning process

The reverse sides were cleaned using 28.4% thioglycollic acid neutralized with ammonia ($\text{HSCH}_2\text{-COOH}$) (pH 7). This solution is a complex forming agent, that is, it dissolves ferric ions in complex form.

Procedures:

1. tamponing
2. soaking with a hygroscopic material soaked in thioglycollic acid
3. mechanical cleaning with scalpel and wire brushes of various hardness, used alternately until a uniform surface emerged; (the extensive corrosion made it impossible to achieve a consistently clean metal surface)

Plate No. 1.

The heavy corrosion had caused the plate to become thin and even perforated in places.

Plate No. 2

The artificially caused magnetic layer persisted in places after cleaning. It came off only in those places where other - more porous and voluminous - corrosion products forced off the rust.

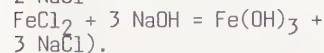
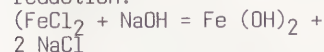
The painted surfaces were cleaned with distilled water containing 1% surfactant (solvate-sulfone-succinic acid ester).

Plate No. 1.

Treatment with 10-15% sorbite solution for about 15 hours (CMC pulp, changing the solution continually). Result: In penetrating the paint layer, sorbite loosened the rust stains, so that they could be removed by gentle rubbing. In some places, where the plate was heavily corroded underneath the rust-imbedded paint, sorbite separated rust from the supporting plate, removing some of the paint in the process, causing only minor losses.

Following cleaning with sorbite, additional local treatment was required for the corrosion spots piercing the paint layer. The distended ferric oxide had to be removed or minimized in order to allow for priming and retouching the losses.

Local electrolysis seemed indicated as the most gentle means of cleaning the spots mechanically. This method also effects reduction:



An "electrolyzing pencil" switched to the + pole emitted an electrolyte solution from a fibre refill to the spot on the plate indicated by the - pole. In places additional mechanical cleaning was needed. The electrolyte solution consisted of 3% NaOH at a voltage of 18 V (5mA).

A more concentrated solution would have damaged the paint layer. The treatment was not considered suitable for the painted surfaces of the plate because the electrolysis would have caused the paint layer to detach from the plate along with the rust.

Once the electrolysis had been completed, the treated areas were washed with distilled water, then carefully mopped with acetone, using cotton held by tweezers.

Plate No. 2

Local treatment with Na-glyconate. Rust stains were treated with Na-glyconate pulped with CMC for about 30 minutes, then washed with distilled water.

Result: The distended rust layer was readily removable using minimal force, causing no damage to the paint layer.

Using solvent solutions described above, old lacquer and oil stains were removed.

As mentioned above, the oil staining the surface probably came from hot drippings from a lamp. The hot oil affected not only the lacquer but the paint as well, making it impossible to remove the oil stain without damaging the paint layer.

Na-glyconate proved sufficiently effective in treating the less corroded plate No. 2. Electrolysis was not needed.



Fig. 4 Detail of icon No. 1 -
before, during, and after
Sorbite treatment

As a footnote to the above, it should be mentioned that as yet no adequate method has been found to completely transform chloride compounds that may remain in objects after cleaning.

Conserving

1. Passivation was achieved by restippling with 10% tannic acid. On painted surfaces tannic acid was applied only as a local treatment because it would otherwise stain the pigments.

2. Coating: PARALOID B 72 was chosen because of its properties regarded as advantageous for both painting and iron support. For coating the rather sizable surfaces of the icons, a relatively slow evaporation was required. This presented a problem in finding a suitable solvent. The paint layer reacted sensitively upon conventional plastic solvents such as acetone, toluene, and chloroform. Finally, a 1.5% solution of PARALOID B 72 in celloxine dilutant was applied to relacquer both sides of the icons. Solvent retention provided for uniform application.

3. Remark: This lacquer coating was intended as a temporary protection for the plates prior to restoration. Once restoration of the support and the paint layer was complete, treatment had to be repeated, this time with a 5% plastic solution. To protect the plates from the high relative humidity in the church, a silicon layer applied to the reverse sides would also be advisable.

Restoration

Complementing the iron support was undertaken with the expectation of 1 making up for losses due to corrosion and 2 reinforcing those parts that had become thinned and weakened in the cleaning process.

In places the iron supports were corroded into a "lace" that could not be complemented simply by stopping up the holes with plastic. The supports had become so flexible that the complements would inevitably fall out over time, even with subsequent restoration. Instead, fiberglass silk patches, 0.2 mm thick, were cut to size somewhat larger than the holes and adhered to the reverse sides with a 5% PARALOID B 72 solution. To strengthen the fiberglass silk material, it was also impregnated with a 20% acetone-toluene solution of PARALOID B 72. Once the patches were fixed in place, an acrylate-type resin (KALLOPAST R - VEB Spezialchemie Leipzig) - coloured with a powder pigment - was stippled on. Using this method, the "patchwork" closely resembled the iron surface, which was darkened by tannin treatment (tannate surface layer). Holes on the painted face of the icon were stopped with a synthetic resin mixture that conformed to the flexibility of the thin iron plate. This mixture, which was stained in the stuff, contained 10 parts of KALLOPLAST to 2 parts of DURACROL (Spofa Dental, Prague). Because it contains a greater amount of filler, DURACROL adds stiffness to the mix.

Losses on the edges were complemented in a similar way. To provide for the additional stress at the edges, two layers of fiberglass silk were applied in these places, coated with a plastic mixture in which the DURACROL content increased toward the surface.

In the course of this treatment the possibility emerged of mounting fiberglass silk on the reverse side of the iron plate, both as reinforcement and as a protective coat. In spite of these advantages, this idea was not implemented because it would compromise one of the primary features of these pictures, namely, that they are supported on iron plates.

Storage suggestions

1. While the cleaning, conservation, and restoration effectively rendered the two icons more resistant to corrosion, they still remain sensitive to the effects of moisture and high relative humidity. A relative humidity of about 40% should be considered ideal for both painting and support.

2. All synthetics used in the restoration are thermoplastic. Direct sunlight should, therefore, be avoided because it could deform the complements.

3. If the icons are to be mounted in ornamental frames, it would be advisable to apply an elastic insert to protect the paint layer covering indented and buckled parts of the plates, since these areas are impossible to repair without damaging the paint.

This restoration effort extended to complementing the iron plates. Overall reconstruction would involve additional priming and retouching to make up the picture losses.

References

1. L. Busi-Benkhardt, "A Grábóci görögkeleti szerb templom ásatási jelentése. (Report on the Excavation of the Eastern Orthodox Serbian Monastery Church in Grábóc) (OMF Archives 25187).
2. A. Fáy, A fémalapok története és használata a festészetben. (History and Use of Metal Supports in Painting) (Thesis, Hungarian School for Fine Arts, 1985/86).
3. R.J. Gettens and G.L. Stout, Painting Materials/Iron (New York: Dover Publications, 1966), 235-236.
4. G. Séd, Régészeti eredetű fémtárgyak tisztítása, konzerválása. (Cleaning and Conservation of Archaeological Metal Objects) (course notebook, Budapest, 1977. MRMK).
5. K. Wahlte, Werkstoffe und Techniken der Malerei (Painting Materials and Technique) (Ravensburg, 1967), etc.
6. Gerhard Banik and Gabriele Krist, eds., Lösungsmittel in der Restaurierung/ICCROM (Solvents used in restoration) (Vienna: Verlag der Apfel, 1984).
7. P. Jánoska, "Avarkori fémleletek kezelésénél szerzett tapasztalatok" (Observations made in treating metal finds from the Avar Age), Proceedings from Museums in Veszprém County (Veszprém, 1983).

ABSTRACT

Esaias van den Velde (1587-1630) is recognized for his role in the development of a more naturalistic and indigenous style in Dutch landscape painting. While his early paintings and etchings are more oblong, one of his earliest signed and dated landscapes (1614) in the collection of the North Carolina Museum of Art measures 25.7 x 31.9 cm. Stechow speculated in 1960 that the sky had been enlarged. In 1986 an in-depth technical study was begun using x-ray radiography, dendrochronology, infrared and ultraviolet photography, and pigment analysis to determine what changes were made to the painting, whether they were by artist or not, and when they might have been made.

The original panel, poplar wood, 12.7 x 31.9cm, was probably 15-16cm in height initially. Oak wood strips have been added to the top and bottom and all thinned and mounted onto masonite in the 1940's. While smalt was the blue pigment in the original panel, the top addition contains ultramarine. None of the dimensional changes are judged to be by the artist, but probably date from the 1800's.

KEYWORDS

Paintings, conservation, Dutch, poplar, oak, masonite, dendrochronology, pigment analysis.

CASE STUDY OF AN EARLY DUTCH LANDSCAPE

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Esaias van den Velde presumably studied under his father, Hans, and also Gillis van Coninxloo who were among a number of artists who fled to Amsterdam from Antwerp after its reconquest by the Spanish in 1585. Another immigrant to Amsterdam was Carel van Mander who published in 1604 *Het Schilderboek*, a three part treatise which includes the lives of artists and a chapter on landscape painting. The development and accomplishments of Dutch landscape painting have been the focus of several important exhibitions in 1986¹ and 1988². Esaias van den Velde is considered a key figure in the development of a more naturalistic style in Dutch landscape painting. Esaias was born in Amsterdam in 1587. In 1609 he moved to Haarlem where in 1612 he was admitted to the guild of St. Luke along with the painters Willem Buytewech and Hercules Segers. They along with Esaias' cousin Jan van de Velde and Pieter de Molijn formed a first generation of new-style landscape painters.

Esaias drew, etched, and painted landscapes, battles, and genre scenes. His earliest dated paintings are from 1614 including two winter landscapes, one in the collection of the Fitzwilliam Museum, Cambridge, and the other acquired in 1952 by the North Carolina Museum of Art, Raleigh (see fig. 1). The Fitzwilliam panel measures 21 x 40.6cm. while the Raleigh painting measures 25.7 x 31.9cm. The more square format of the painting was questioned in 1960 by the art historian Wolfgang Stechow³ who recognized the significance of the painting as early as 1947 and then later speculated that the sky had been enlarged to accommodate a change in taste. Such was the case for several oblong landscapes by Hercules Segers (c.1589/90 - c.1638). While subsequent scholars assumed the enlargement of the Raleigh painting was true, it was not until 1986 that an in-depth technical study was begun with x-ray radiography and an attempt at dendrochronology. The focus of the study was to determine what changes were made to the painting both in size and composition, whether they were by the artist or not, and when the changes might have been made.

George S. Keyes, author of the monograph on Esaias⁴, sees strong connections among the oblong formats of the early paintings, drawings, and etchings.⁵ For example, among the drawings illustrated in the Keyes book are numbers 15-22 which were done as preparatory studies for etchings and which average 73-169mm. The dimensions of the Fitzwilliam painting set a height to width ratio of 1:2. A panel in the Rijksmuseum entitled *The Ferryboat* was found to be increased in height by 14cm.⁶ Its original dimensions would have been 61.5 x 113cm, which is also a ratio of 1:2.

When the Raleigh painting was x-ray radiographed (see fig.2) it became apparent that the support consisted of 3 separate sections of wood having a horizontal grain. The lowest measures 1.6 x 31.9, the middle is 12.7 x 31.9, and the top is 11.4 x 31.9cm. This fact had not been noted before because all three had been thinned to 0.1cm. and mounted onto 0.6cm. (1/4 inch) thick masonite which was veneered with oak and cradled. All four edges were veneered with oak to hide the lamination. Dr. Peter Klein of Hamburg University in 1986 attempted to date the wood by means of dendrochronology but could not due to its thinness. He did confirm the top and bottom sections to be oak and identified the largest in the center to be poplar. It is the poplar section which is believed to be the remnant of the original support.

Oak wood is the expected support for Dutch landscape paintings when wood is used. Keyes lists 187 paintings of certain attribution to Esaias. One hundred and sixty-four are on panel while twelve are on canvas. When wood type is identified, fifty-seven are listed as on oak. Catalogue #134, a 10.7 x 19.3cm landscape in a private collection is listed as softwood.

That the Raleigh painting or other small Dutch panel paintings are not on oak wood is apparently not unusual. Bauch and Eckstein⁷ have reported that while Rembrandt used mostly oak wood while working in Leiden, after moving to the import city of Amsterdam he began using other wood species including walnut, poplar, redbeech, cedrela, and mahogany. The patents for the manufacturing process of masonite by steam treating and pressing wood fibers were issued to William H. Mason of Laurel, Mississippi, in 1926, 1928, and 1938. Therefore the thinning of the panels and the mounting onto masonite must have taken place in the United States in the late 1940's. The painting left a German family collection after World War II and was purchased by the North Carolina Museum of Art in 1952 from a New York dealer. What needed to be determined was, how large was the panel originally and did Esaias have anything to do with the enlargement.

By examining the endgrains of the panels, it was apparent that all three had been painted upon at the present width because paint rounded over them. There was no

evidence of cutting or sawing which would leave fractured paint. There is such evidence in the radiographs between the horizontal joins in the three panels. It is logical to assume then if new panel sections were added to the top and bottom edges of an older panel, some of the latter would have to be trimmed to make a clean, straight joining edge. This may well be the case of the Raleigh panel. The radiographs also show rounded corners between the poplar and top oak panels. At the right edge this join shows differential wear causing mis-matched irregularities on the vertical edge. The fact that there is no known precedent for two different woods in the same panel and that the end grains show different wear patterns reduces the possibility that the current structure dates from 1614. If one were to apply the 1:2 height to width ratio discussed earlier to the opinion that 31.9cm is the original width, than the original height was approximately 15-16cm.

There are three universally accepted landscape paintings by Esaias' Haarlem contemporary, Hercules Segers. According to Dr. Jan Kelch⁸ of the Gemäldegalerie in Berlin, all three are on oblong oak panels and all have been enlarged. Dendrochronology on Village by a River originally 12.8 x 36.1cm and enlarged to 26 x 36.1cm and View of Rhenen originally 22 x 66.6cm and enlarged to 42 x 66.6cm shows that the additions could have occurred as early as 1640 when they were owned by an Amsterdam art dealer. The original paintings date c.1625/30.

To determine whether the changes in the Raleigh painting could have been made later in his career, later in the 17th century after his death in 1630, or in more recent times, a study of the paint and ground layers is important. Infrared photography (see fig.3) shows the paint over the top oak panel to be darker than that over the poplar. The paint over the bottom strip of oak does not stand as much in contrast to the original painting. Ultraviolet/visible fluorescent photography showed a variety of retouched areas, particularly over the joins, under a strongly fluorescing varnish. The paint over the poplar panel gives the impression of greater age than that over the oak sections due to a much more extensive mechanical crack pattern. While there is a fine network of mechanical cracks in the upper section of sky giving the impression of at least 100 years of age it is difficult to believe that it is 375 years old. It has no damages which required retouching whereas the section over the poplar wood, when carefully examined under the stereo-microscope, has much re-painting over old cracks.

The infrared and x-ray studies do indicate a surprising number of changes in the small composition. The man of the couple at the left was positioned more to the right. The couple on skates in the central foreground was originally positioned higher. There may have been a pair of skaters under the bridge. All of the buildings appear to have undergone either a height increase or roof-line changes.

The most interesting changes appear in the large tree at the extreme left. The tree is painted as though it has been pruned back to the main trunk or it has died and lost most of its branches. There are precedents for this type of truncated tree form in drawings and etchings by Esaias. Both infrared photography and infrared reflectography suggest pentimenti of branches extending into the sky over the poplar and oak supports. The top of the tree trunk does extend across the join. The paint at the top of the tree shows dark in the infrared photograph suggesting it is later and was used by someone to visually unify the panels. The radiograph suggests a darker (less dense) reserve for the tree trunk stopping 0.5cm short of the join line.

While many design changes are noted, no underdrawing, that is carbon black lines, could be detected. In the 1986 catalogue of the exhibition at the National Gallery, London, David Bomford published an infrared photograph of another Winter Landscape by Esaias (cat. no. 66).⁹ Here the conditions of a carbon black drawing on a light-colored ground layer made the infrared image possible. The poplar panel of the Raleigh painting does not have such a ground, but rather black pigment (with some yellow earth) has been rubbed into the wood grain. The darkened wood may have been left exposed to serve as middle tones for shadows and reflections of the buildings on the ice. It is interesting to note here that a similar technique was used by the slightly later Dutch "Tonal Landscapists" Jan van Goyen (1596-1656) and Salomon van Ruisdael (1600/2-1670).¹⁰ Jan van Goyen was a student of Esaias in Haarlem. The later painters deliberately permitted the tone of their wood supports to show through a transparent ground of white lead and chalk.

The oak panel sections of the Raleigh painting have thick grounds which are warm grey in color. It is this single layer which is caught in the oak wood grain and which is so evident in the x-ray radiograph. Polarizing-light microscopy by the author indicates the ground to be largely white lead with some earth color. The sky tones in the poplar and oak sections are applied directly to the ground layers based on cross-sectional studies. To return to the branches appearing as pentimenti in the sky over the oak section, cross-sectional studies indicate they are brown lines painted directly on the grey ground and under the one and only blue layer of the sky.

A photograph of the Raleigh painting was published in 1911¹¹ when it was in a Munich collection. A difference in the condition of the paint over the upper join line is

more visible there than now. The one obvious change is the tree branches seen growing from the sawed-off limb on the right side of the tree. These limbs can be seen in the infrared photograph. While the repaint over the branches is resistant to acetone and even dimethyl formamide solvents, it must have been applied after 1911. It is possible that much of the visible retouching was done in the 1940's when the panels were thinned and mounted onto masonite.

In order to search for some basic difference between the paint of the original blue sky over the poplar and that over the oak section, a study of the blue pigments was undertaken. By means of polarizing-light microscopy, isotropic particles having a ground glass appearance were judged to be smalt. The presence of cobalt, silica, potassium, and aluminum as detected by electron microprobe analysis¹² supported the identification of cobalt blue pigment. It is a color well-documented in 17th century Dutch painting.¹³ Van Mander advises to "even show a completely clear sky with the purest blue of azurite or smalt at the top."¹⁴ It is interesting that he does not mention ultramarine blue. Gifford did not find any in her previously cited study. Small isotropic and rounded particles were found dispersed and in agglomerates within a matrix of white lead and were judged by means of polarizing-light microscopy to be artificial ultramarine blue. This blue pigment was not available until 1830.

Stylistically the formulation of the clouds in the sky also suggests origins in the nineteenth century. Dr. Anthony Janson, Chief Curator of the North Carolina Museum of Art considers the extended sky similar to those seen in German landscape painting from the second quarter to mid-nineteenth century. The artists involved are generally minor painters scattered throughout Germany who imitated Dutch landscape painting and the French Barbizon school.

In summary, because of the materials, condition, and the handling of the blue paint in the sky on the top addition, it is proposed that the enlargement was done in the nineteenth century, rather than in the seventeenth century as was the case of the Segers oblong panels. Following the 1:2 height to width ratio used by Esaias during his early work, it is proposed that 2.3 - 3.3cm of the original poplar panel was cut off at the top. The original dimensions of the panel were probably 15-16 x 31.9cm. The extra space may have provided room for Esaias to paint the branches which appear as pentimenti in the sky over the added oak section. The brown painted lines cannot be original, but may be an underpainting test by whomever may have trimmed the original panel and added the oak sections. This person may well have had the last opportunity to see how Esaias had resolved the tree as a compositional element. That there are so many changes by the artist in the original composition suggests that he assigned much importance to achieving a resolution. At this time there is little technical evidence on Dutch landscape painting from the early decades of the seventeenth century. It is hoped that the above study will contribute to a better understanding of this important phase in the development of landscape painting.

NOTES

¹Christopher Brown, Dutch Landscape, The Early Years, Harlem and Amsterdam 1590-1650, a catalogue published with an exhibition held at the National Gallery, London, September 3 - November 23, 1986.

²Peter Sutton, Masters of 17th Century Dutch Landscape Painting, an exhibition catalogue (Boston: Boston Museum of Fine Arts, 1987).

³Wolfgang Stechow, Dutch Landscape Painting (Oxford: Phaidon Press, 1966), 87.

⁴George S. Keyes, Esaias van den Velde (Doornspijk, The Netherlands: Davaco, 1984).

⁵Conversation with the author, October 20, 1989.

⁶Sutton, *op.cit.*, p.499.

⁷J. Bauch and D. Eckstein, "Woodbiological Investigations on panels of Rembrandt Paintings," Wood Science and Technology XV (1981), 251-263.

⁸Letter to the author, October 27, 1989.

⁹C. Brown, *op.cit.*, 52-53.

¹⁰E. Melanie Gifford, "A Technical Investigation of Some Dutch 17th Century Tonal Landscapes," Preprints, American Institute for Conservation Annual Meeting, 1983, 39-49.

¹¹Von Herman Nasse, "Gemälde aus der Sammlung des Univ.-Professors Dr. Freih.Fr.W.von Bissing zu München," Münchener Jahrbuch der bildenden Kunst, Vol.6, 1911, p.97, ill.17.

¹²Electron microprobe analysis and x-ray diffraction were conducted on samples by Inge Simonsen at the Analytical Instrumentation Facility, Department of Materials Science and Engineering, North Carolina State University.

¹³Gifford, *op.cit.*, 39-49.

¹⁴A translation of Carel van Mander's (1604) Chapter Eight of Den Grondt der Edel Vry Schilderconst appears in the 1986 National Gallery, London, catalogue, 36-43.



Fig. 1 Winter Scene (1614) by Esaias van den Velde. North Carolina Museum of Art (52.6.61)

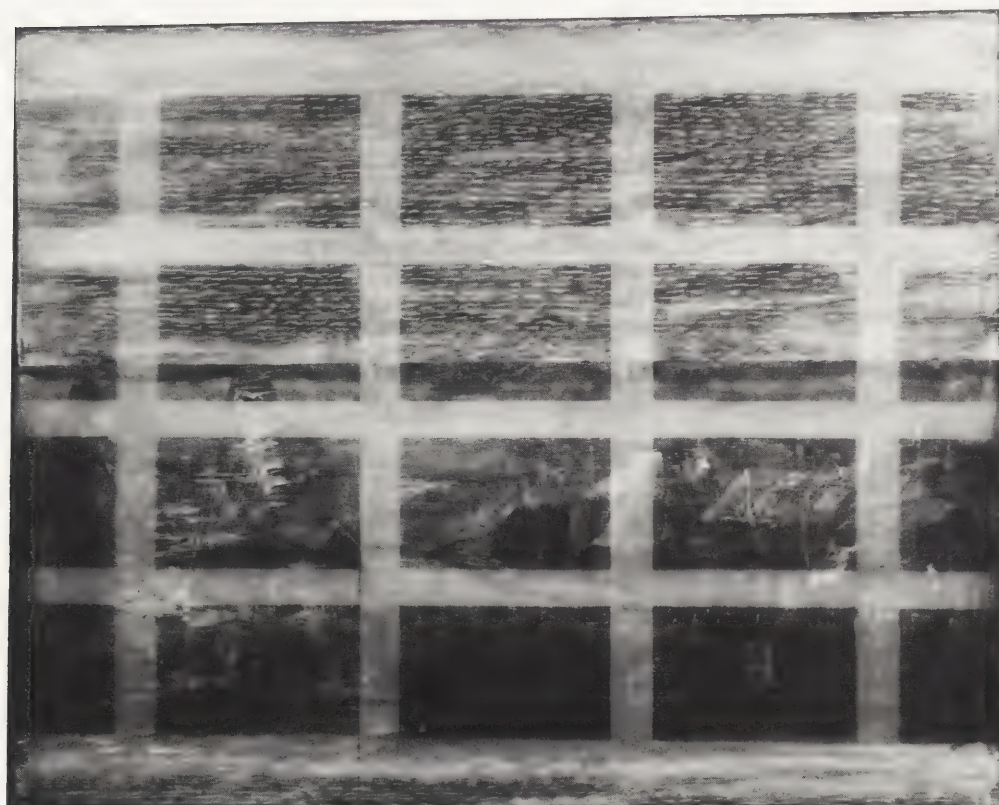


Fig. 2 Winter Scene, x-ray radiograph, 20KV, 3MA, 90 seconds.



Fig. 3 Winter Scene, infrared photograph.

ABSTRACT

The method worked-out at Grabar Conservation Centre of conservation of Oriental lacquers. Historical reference on Vietnamese lacquerwares. Consolidation treatment. Completion of losses, toning.

KEYWORDS

Conservation, consolidation, lacquers, mastics, solvents.

THE METHOD USED FOR CONSERVATION TREATMENT OF THE VIETNAMESE LACQUER SCULPTURE "DONATOR"

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The sculpture was badly damaged: it was covered with numerous cracks and scratches, we could watch the losses of the lacquer layers, considerable peeling away from the wooden support, isolated cases of the lacquer exfoliation, numerous removals; the foundation of the sculpture had burst all over its length. We were forced to work out the method to solve the problem bearing in mind the fact that there were no ready methods used for realization of the conservation treatment within the range of the world conservation practice.

The Oriental lacquer comes from the sap of the tree *Rhus vernicifera*. Under climatic conditions of the tropics the lacquer has been in mutual use for ages as an indispensable material applied to protect wooden and leather objects from influence of moisture (we know the cases when the objects have preserved the original qualities after their long-term sojourn under water). Later on, the lacquer came into use as a decorative coating on the objects made of various materials (silk, stone, etc); its splendid decorative qualities were of world wide repute.

The written information concerned with the technology of the lacquers' preparation is at variance. Even the Vietnamese masters, such as Fphan-Ke An, LeTkhân Duc and others, describe the process unequal way as well as the artist Nguyễn Xuân Cuong who trained the conservators including the author of the present paper. Applying the traditional materials the master has taught his students the technique of the lacquer painting - as far as it was possible - and demonstrated them the process of the traditional Vietnamese conservation treatment (or, more precisely, the repair).

Resinous sap of the trees collected inside the special vessels was poured into bamboo baskets which had been covered with layer of paper and coated with varnish and silt. The resin was allowed to stay inside a room, after this process the former has separated in several layers.

Let us consider these layers from top to bottom.

1. "Oily" - resin 90% conc. Dries badly, dark in colour, fluid. Before use this layer should be diluted with the other one.
2. "1st sort" - resin 70% conc. Not so fluid, yellow-pink in colour, aromatic smell. Before use should be diluted with the "oily" layer.
3. "2nd sort" - resin 60% conc. Dense, light in colour. Before use the layer should be blended with silt to obtain the ground. When being diluted with "oily" layer the lacquer of rough quality is obtained to be used as a coating of the support. The "2nd" sort layer is of use as an adhesive.
4. "flesh sort" (or "honey" one) - resin 50% conc. Denser, light

in colour. The "flesh sort" layer is of use for grounding boats, vessels, etc.

5. "tin water" - resin 40% conc. No use.

The lacquer ready for use is manufactured by agitation the layer "1st sort" with wooden or iron small stick (as a rule, the "1st sort" layer is diluted with the "oily" one to improve the quality of the ready production). There are two kinds of the lacquers ready for use: the brown lacquer ("kanzan" - the colour of the cockroach wings) and the black lacquer. The brown one is manufactured by agitation the lacquer with wooden small stick during 20 hours (30-35 rotations within a minute) as well as over the influence of oxygen. This lacquer serves a medium for the paints' preparation. The black layer is manufactured by agitation the lacquer with an iron small stick (as well as inside an iron pot): by combining with ferroferric oxid the lacquer turns black in colour. The red lacquer is manufactured by means of cinnabar blended with vegetal oil.

Gold and silver were also used for manufacturing lacquer-ware. Due to the fact that the Vietnamese easel painting in lacquer developed, in 1930s, the local masters started working with the other materials by blending colophony and resin. Refined and processed lacquer was brushed over various surfaces by several layers (up to 100 layers over the carved objects), and every layer was allowed to stay for a long term to dry. The process of the lacquer hardening needs very humid environment.

Quite apart from the fact that the technology of the lacquerwaremaking suggests layer after layer application of the coating, in the course of time the ecclesiastical sculptures suffered numerous renovations when the colouration qualities of an object were not sometimes taken into consideration.

To promote the consolidation treatment we determined all the types of damages characteristic of the lacquers.

The types of damages

Mechanical damages (snabby areas, scratches, etc), cracks in the lacquer surface and those in the wooden support, peelings of the lacquer layer, removals, warp, bubbles between the lacquer coating and support, unevennesses.

The distinctive features of the Oriental lacquer are not characteristic of the other known kinds of varnishes; the fact that complicates its treatment. This one is dissolved and softened with no known solvents. While an object is stored under stable environment its lacquer coating is quite firm and safe. But when the temperature-dampness regime changes the lacquer film turns very brittle, exfoliates and removes from the support when slightly touched. Sometimes it happens that the lower layers of the lacquer and the ground tend to remove despite the fact that the outer layer shows its good state of conservation. Thanks to this circumstance it is absolutely impossible to run through the upper layer using a needle: the former cracks right away. It is impossible to lift a peeled fragment of the lacquer even slightly without break as well. These factors cause numerous difficulties which appertain to the process of

consolidation.

The first attempt to use levkas (chalk ground) and cold setting adhesive for consolidation treatment has failed; the result was just the same as that reached by our colleagues from the Museum of Oriental Art in Berlin. As for levkas, one should remember: bubbles should be fully filled up with fluid levkas within a very short period of time (This is practically impossible), otherwise hardened levkas will prevent its additional portion from penetration inside the bubble. As for PVA dispersion, when hardening the adhesive shows volume shrinkage and spreads over the support and inner surface of a bubble reducing to films, so the cavity between the newly generated films remains hollow, if the lacquer is strong. But if the lacquer is brittle and thin, the adhesive pulls it up to the surface - the lacquer layer cracks. As a matter of experience, we want to give off an interesting nuance that denies use of the above-mentioned materials. In our case it is well seen under the microscope that the coloured lacquer coating on the face numbers about 10 layers as well as the red lacquer coating on the garments numbers 8 layers. When hardening the adhesive (which shows volume shrinkage) can pull up one or several layers that have partially lost their cohesiveness in the course of time. So the inner texture of the lacquer coating will be broken, hence its strength will diminish even more. Moreover, enumerated materials stick the lacquer badly.

Use of fish-glue brought no results (excluding some characteristic damages). This adhesive sticks the lacquer badly as well. Wax-resin mastic proved to be the most suitable material amidst those testified. The fact that it is possible to achieve plasticizing of the lacquer under the influence of heat served the telling argument for benefit of the mastic. This point is of great value when considering the problem of conservation treatment.

Here we are recording the process of the conservation treatment.

Tools and materials used: spatula (warming and fluoroplastic), steel needle, syringe with electric heater (for mastics with various melting points), thermal screen, alcohol, benzine, fish-glue, components of mastic.

We started our treatment with consolidation of the lacquer layers in the areas of the face and hands: here the state of the lacquer conservation was archbad. Every anwary touch and even vibration could cause removals.

Now we want to provide some information concerning the softening point of the materials; when working we used the mastic prepared to carry out our consolidation treatment. (That is not a traditional mastic used in painting conservation.)

If the lacquer plasticizes at a certain temperature, one should choose a mastic which allows the lacquer to heat till it is necessary, shows stability not penetrating into wooden support, while the lacquer shows stability not being burnt down at a softening point of a mastic.

Due to the fact that the temperature of plasticization of the lacquer layers applied on the different areas of the sculpture differs it is clear that in the first instance it is necessary to bring into proper correlation (1) the temperature of the lacquer plasticization (the temperature of the air when the lacquer plasticizes) and (2) the melting point of the mastic. (For instance, the red lacquer: t° of plasticization is $45-50^\circ\text{C}$, $t^\circ 60^\circ\text{C}$ is optimum for the procedure of laying; the white lacquer: t° of plasticization is 50°C , $t^\circ 50^\circ\text{C}$ is optimum for the same procedure.)

Thus we have studied the surface of the sculpture to choose the adequate mastics to treat its different areas and compounded the three kinds of mastics - low-melting, high-melting, mid-melting. We used synthetic wax to obtain the mastic with melting point over 45°C .

The face and hands of the sculpture had suffered renovation with white paint. The paint had been brushed over the layer of pink lacquer which differed from the other lacquer layers applied over the other areas of the figure. Under the microscope we could see the nacre tinges; the upper layer of this lacquer coating was low-melting. As it seems to us, the problem arises from the fact that this distinguishable layer was brushed during the course of the previous conservation. This pink layer had been manufactured by means of both lead white (though the Vietnamese used to take advantage of titanium white) and, likely, nacre powder, as evidenced from the chemical analyses. This lacquer showed very low adhesiveness, that is why the damages on the face and hands were the worst. Besides, the lacquer was guttered.

For consolidation treatment we used low-melting mastic by sticking on it the removed parts of the pink lacquer. We treated the rest of damages by means of the mastic. We distributed it inside the cracks and losses of the lacquer, then heated it with spatula and thermal screen. As a result the mastic has penetrated into all parts of the lacquer and consolidated it. As for the consolidation treatment of the lacquer coating in the area of the garments, we carried out it as follows. At first we filled up the bubbles between the lacquer coating and the support by means of the mastic using syringe with electric heater (our own construction) and then laid the lacquer with spatula manipulating over the protective film.

The lacquer should not be heated strongly taking into consideration thermochromism (over 100°C). Therefore, it is necessary to bring into proper correlation (1) the temperature of the mastic, (2) the temperature of the lacquer, (3) the temperature of the spatula. Thus at a touch of the spatula the lacquer must yield not showing thermochromism; on the other hand, if the upper coat of the mastic is melting, the lower ones must remain harden. In the first instance this statement is concerned with the treatment of the warped areas.

When carrying out the consolidation procedure one must take into account a complicative circumstance: the specific character of the lacquer prevents from injection of mastic upon

some damaged areas by means of the traditional tools, such as syringe or so. As the case stands, when injecting the consolidant we had to apply the peculiar method. To remedy the arched cracks with the raised lacquer layer we used the powdery high-melting mastic. The mastic was inculcated as deeply as possible (such cracks allow to fulfil this operation) and then smoothed with the heated spatula.

Taking into account that the lacquer was brittle it was necessary to undertake its additional consolidation treatment for the temporary protection (sometimes the lacquer tends to crack when slightly touched). For the first time in the conservation practice we used a new method of multi-functional preventive sealing. Depending on a character of cracks we spreaded a layer of thermostable silicon over the lacquer layer. In addition this newly generated silicon film protected the lacquer surface from the direct contact with heated spatula. Use of silicon is harmless: we've kept a silicon coating on an experimental item half a year.

We carried out consolidation treatment of large amount of cracks and peelings of different types and configurations using the mastic with different melting points by injecting its hot portions under the lacquer layer with syringe; when it was necessary we drove away the mastic with heated spatula. Herewith the silicon coating prevented the mastic from running out of the adjacent cracks.

To consolidate the accessory areas of the sculpture - their position allowed to undertake perforation not damaging outward appearance of the object - we also took advantage of thin silicon coating to inject the mastic under the lacquer layers with syringe. When one wants to perforate the protected lacquer with hot needle, silicon distributed heat a way to avoid thermochromism of the lacquer in the areas around the openings (such accidents always take place without presence of protective coating). When carrying out such an operation it's necessary to plan the definite sequence of the injections to be done in order to avoid repeated heating of the lacquer surface in the course of which new damages will occur.

As for the treatment of the "kanzan" lacquer layer (yellow in colour, liquid lacquer coated over the silver paint in order to imitate gold; the method similar to that of the khoklomawares), we carried out it as follows. The thin lacquer layer was very brittle, warped, with numerous large losses and peelings in all places. Under the lacquer layer we injected alcohol followed by fish-glue (from 6 to 12% conc.) and laid the lacquer with heated spatula.

The problem concerned with the treatment of the bubbles without cracks is worthy of special note for lack of the natural inlets to fulfil the procedure of filling in the course of which even surface will suffer damages caused by perforation. No means are known to blot out these newly generated openings, but, sooner or later, we hope, the solution of the problem would be found. Moreover, for lack of cracks the lacquer is sufficiently firm and shows stability for a long

time.

Completion of losses

When seeking for the materials suitable to carry out the the completion of the lacquer fragments we were bound up with the hard-and-fast rules of the museum conservation making provision for reversability of the materials, their diversity in comparison with the original as well as their capacity for outward imitation of the exhibit. As is usually the case, one solves the problem by resorting to the help of the various generally used coating varnishes for imitation of the surface.

To fulfil our treatment we took advantage of the method similar to encaustic. We had blended wax-resin mastic with pigments and then filled up the lacunae the way as following from the original colour of the lost fragment of the lacquer by means of the hot method. The layer of this cool paint mass bears a very close outward similarity to the lacquer surface. From now on there is nothing for it, but to polish the completion to a certain degree. Such being the case, one should apply the mastic by turns (layer after layer) by which means to avoid cracks caused with hardening.

We completed small cracks and other damages by means of wax, toned those areas making use of water colour, then polished them with wax.

REFERENCE

We started our elaborations in 1985. When we were close to gain of our aim, the author acquainted with the information by Mrs Anita Franke concerning the elaboration of the same problem at the Berlin Museum of Oriental Art (since 1976th). Although the work was carried out independently, the results occurred of the similar nature.

RESUME

Les cadres et supports flamands des 15e et 16e siècles sont souvent essentiellement fonctionnels. Ce sont des éléments du mobilier, conçus et construits par les menuisiers, mais aussi par les charpentiers, sculpteurs et huchiers, parfois même les tourneurs. Le bois de chêne était débité et mis en oeuvre de manière à limiter les effets du jeu du bois. Les modes d'assemblages des planches entre elles, des éléments du cadre et également du panneau au cadre, étaient très variés et témoignent d'une tradition et d'un métier soigné. La destination de l'oeuvre (retable d'autel, domestique, oeuvre à suspendre ou à poser) explique certaines particularités de la construction. Par ailleurs ont joué également le souci qu'avaient les menuisiers de l'efficacité et de la rapidité de leur travail. L'évolution du goût a eu pour conséquence une évolution dans la mouluration et dans la forme.

MOTS-CLES

Cadre, support, assemblage, embrèvement, battée, tenon et mortaise, queue d'aronde, enfourchement, mi-bois, entures, onglet.

ASPECTS TECHNOLOGIQUES DE L'HISTOIRE DE LA PEINTURE FLAMANDE : CADRES ET SUPPORTS AUX 15e ET 16e SIECLES.

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Introduction

Les cadres du 17e siècle hollandais ont fait l'objet d'une importante exposition et d'un excellent catalogue (1). Nous avons consacré récemment un ouvrage aux cadres et supports flamands des 15e et 16e siècles (2). On mettra ci-après en évidence certains aspects peu connus de la question.

L'intérêt actuel pour les supports trouve en partie son origine dans des problèmes de conservation. Le mauvais état du support est une cause de détérioration des oeuvres de peinture. Les cadres originaux subsistent en grand nombre, mais ils sont souvent ignorés parce que manquent les critères de datation et qu'ils sont surpeints et défigurés par des restaurations abusives.

Aux 15e et 16e siècles le support est conçu comme une pièce de menuiserie, panneau et bâti, construite de manière très fonctionnelle. Les menuisiers, les charpentiers, les sculpteurs ou huchiers et, occasionnellement, les tourneurs, ont produit les supports de peinture. Ce n'est qu'au 17e siècle, avec le succès grandissant des supports de toile, que naît une nouvelle conception du cadre, le cadre cachant ou ornant le bord des peintures.

L'aspect final du cadre n'est pas négligé par l'artiste qui, parfois, surtout au 15e siècle, le décore de sa main, l'inclut dans son oeuvre, y porte date, signature ou autres inscriptions. Dans d'autres cas, le cadre est mis en couleurs de manière assez stéréotypée, mais le plus souvent en couleurs vives : rouge, vert, bleu. Au 16e siècle, la polychromie noir et or prédomine. Paradoxalement, il semble que cette simplification ait été de pair avec le développement du décor mouluré ou sculpté dans le cas où s'introduisent des éléments renaissants.

Les présents résultats sont basés sur une large enquête menée dans les principaux musées de Belgique et portant sur les oeuvres exposées et conservées dans les réserves. Il s'agit des musées suivants : à Anvers : *Museum Mayer van den Bergh* et *Koninklijk Museum voor Schone Kunsten*; à Bruges : *Groot Seminarie*, *Sint Jans-Hospitaal*, *Stedelijke Musea* et *Potterie*; à Bruxelles : les *Musées royaux des Beaux-Arts de Belgique*; à Gand : *Bijloke Museum*, *Sint-Baafs Kathedraal* et *Museum voor Schone Kunsten*; à Kuringen : *Abdij Herkenrode*; à Louvain : *Sint-Pieterskerk* et *Stedelijk Museum*; Malines : *Openbaar Centrum voor Maatschappelijk Welzijn*; Namur : *Musée Gaiffier d'Hestroy*; Sint-Truiden : *Seminarie*; Tongeren : *Onze-Lieve-Vrouw Basiliek* et *Stedelijk Museum*; Tournai : *Musée des Beaux-Arts*.

Essence et débit

Sauf rares exceptions, le bois utilisé par les maîtres flamands est le chêne. Une partie de ce bois au moins était importée de la Baltique. La grume était débitée en quartiers probablement sur les lieux de l'exploitation. Quelques supports circulaires sont d'un autre bois, ce qui s'explique par le fait qu'ils sont produits par les tourneurs. L'usage du chêne leur était interdit.

Le débit des quartiers de grume se faisait sur mailles (sur quartier) pour éviter au maximum le jeu du support soumis aux variations climatiques. Ce débit pouvait se faire à la hache ou à la scie, la première de ces deux manières étant la meilleure car elle ne sectionne pas les fibres et garde au bois toute sa solidité.

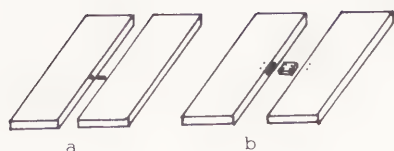
Souvent cependant les éléments du support furent taillés à la scie. Ce procédé était le plus économique et d'une plus grande efficacité notamment pour la longueur des planches. Les cadres, constitués d'éléments de plus forte épaisseur, sont toujours composés de pièces sciées.

Assemblage du support

Lorsque les dimensions de l'oeuvre le permettent, le support est constitué d'un seul élément. Ordinairement, deux ou plusieurs planches forment le support d'une peinture flamande.

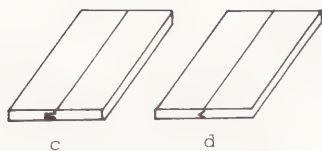
L'assemblage à joint vif se rencontre dans près de 90% des peintures depuis la fin du 14e siècle jusqu'au début du 17e siècle. Le plus souvent, le joint vif est renforcé de tourillons, pièces de bois plus ou moins cylindriques

insérées parallèlement au champ du support et maintenues dans des encoches ménagées à cet effet dans les rives de chaque élément (fig. 1.a).



a

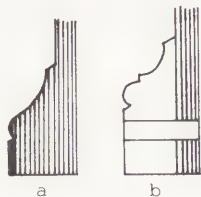
b



c

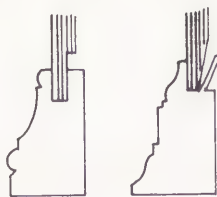
d

fig. 1.a : assemblage à joint vif renforcé d'un tourillon, b : assemblage à joint vif renforcé d'une clé, c : assemblage à rainure et languette, d : assemblage à grain d'orge.



a

b



c

d

fig. 2.a : cadre taillé dans la masse, b : cadre appliqué, c : cadre rainé, d : cadre à battée.

Dans des oeuvres de grandes dimensions, la clé peut remplacer le tourillon (fig. 1.b). La clé est une sorte de tenon de bois de quelques centimètres carrés inséré dans les rives des éléments du support et maintenu le plus souvent par deux ou quatre chevilles transversales affleurant ou non la face. Dans le courant du 16^e siècle, certains grands panneaux sont assemblés à joints vifs avec clés non chevillées.

L'assemblage à rainure et languette est relativement fréquent au 16^e siècle, mais il apparaît souvent dans des oeuvres d'intérêt local et de qualité médiocre (fig. 1.c).

D'autres assemblages - moins souvent rencontrés - sont également à distinguer de l'assemblage à joint vif. Il s'agit de divers types d'embrèvements, où, comme dans l'assemblage à rainure et languette, il y a pénétration d'un élément dans l'autre. L'assemblage à grain d'orge est notamment adopté pour assembler un élément horizontal à des éléments verticaux (Rubens, *Triptyque de la Descente de croix* (1612), volets, Anvers, cathédrale) (fig. 1.d).

Assemblage du support au cadre

Cadres et supports taillés dans la masse (fig. 2.a) se rencontrent surtout aux 14^e et 15^e siècles pour les petits panneaux cintrés constitués d'une pièce unique ou exceptionnellement de plusieurs éléments.

Le cadre appliqué est chevillé (rarement cloué par le revers), sur une des faces du panneau, l'autre face restant plate. On rencontre cette manière de faire dans les volets de retables ou dans des panneaux sans volets. Cet usage était peu approprié à une menuiserie portante. Il reste en vigueur jusqu'au 17^e siècle (fig. 2.b). Une variante ancienne de ce système existe dans les autres cadres partiellement taillés dans la masse, partiellement appliqués. Les montants, dans le sens du fil du bois, sont taillés dans la masse et les traverses indépendantes sont chevillées au support dans l'*Homme au turban* (1433) de Jean van Eyck (Londres, *National Gallery*).

Jusque vers 1520, le panneau est généralement embrevé dans le cadre rainé (fig. 2.c). Le panneau élagé sur les bords s'insère dans une rainure qui le maintient fermement mais permet au jeu inévitable du bois de se réaliser. Après 1520 et pendant tout le 16^e siècle on peint dans ou hors cadre, selon les exigences pratiques. Les deux systèmes peuvent intervenir simultanément chez le même artiste.

Le cadre à battée apparaît peu avant 1520 (fig. 2.d). L'usage de la battée se généralise vers le milieu du 16^e siècle et est toujours en usage de nos jours. Le panneau s'appuie contre la battée au bord intérieur du cadre et est maintenu par des chevilles de bois, ou, le plus souvent, par des clous forgés.

Des éléments de renforcement sous forme de traverses ou de barres existaient au revers de nombreuses oeuvres de grandes dimensions surtout celles destinées à porter le poids des volets. L'étude de la *Descente de croix* de van der Weyden (Madrid, Prado) a mis en évidence les traces d'un système élaboré de montants et traverses arrières aujourd'hui disparu. Cette construction semble conçue pour permettre au cadre de résister à un poids important, celui des volets (3).

Assemblage des éléments du cadre

Nous avons relevé, pour les assemblages des éléments du cadre une quarantaine de variantes qu'on peut classer en six grandes familles : les tenons et mortaises, les assemblages à queue d'aronde, les assemblages à enfourchement, les assemblages à mi-bois, les assemblages à éléments rapportés. Un dernier groupe d'assemblages est constitué par les entures ou assemblages de pièces mises bout à bout, utilisées souvent pour joindre les parties cintrées des cadres aux montants.

L'assemblage à tenon et mortaise à coupe droite fut adopté dans certains cadres de van Eyck, notamment dans les cadres du registre inférieur de l'*Agneau mystique* (fig. 3.a). Cet assemblage solide et de réalisation simple présente néanmoins l'inconvénient de rendre difficile la réalisation de la moulure dans les angles. En effet, il fallait tailler au ciseau l'angle de la moulure dans une pièce et réaliser donc un travail à contre-fil. Les assemblages présentant une coupe mixte solutionnent ce problème et améliorent la disposition de la moulure.

L'évolution qu'on observe dans les assemblages depuis la fin du 15^e siècle doit se voir en relation avec le développement du décor mouluré, au départ toujours simple et souvent confiné à l'arête intérieure du cadre. L'onglet allié à un assemblage solide permet un alignement heureux des moulures et un travail à l'air libre des guillaumes (rabots à moulurer) poussés d'un bout à l'autre des pièces. On voit la coupe d'onglet adoptée dans l'*Homme au turban* de Jean van Eyck (1433), Londres, *National Gallery*, dont il a été question plus haut. La recherche des menuisiers portera sur la combinaison de l'onglet avec

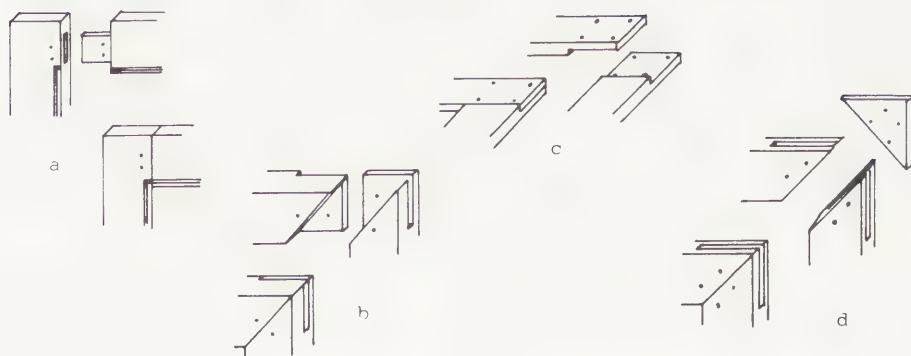


fig. 3.a : assemblage à tenon et mortaise. b : assemblage à enfourchement arasé d'onglet sur un parement. c : assemblage à mi-bois. d : assemblage à clé.

un assemblage solide et donnera lieu au cours du 15^e siècle à une variété d'assemblages souvent complexes dont certains sont caractéristiques de l'un ou l'autre centre de production.

Au 16^e siècle se généralise dans tous les centres l'usage de l'assemblage à enfourchement arasé d'onglet sur un parement (fig. 3.b). Facile à réaliser, jugé suffisamment solide, il permettait un alignement heureux d'une mouluration de plus en plus développée. L'origine de cet assemblage semble devoir être cherchée dans la menuiserie bruxelloise. Peut-être dérive-t-il de la menuiserie des retables sculptés.

L'assemblage à mi-bois est adopté pour la partie intérieure de cadres doubles, notamment dans la production des Francken à Anvers dans la seconde moitié du 16^e siècle (fig. 3.c). Pour un cadre extérieur, l'assemblage à mi-bois est rare. Exceptionnellement, un cadre peut ne pas être chevillé et seulement collé. Un assemblage à clés peut unir en son sommet les deux parties d'une traverse cintrée (fig. 3.d). L'exemple le plus précoce de barres d'angles que nous ayons pu observer date de 1610.

Outre les avantages techniques que fournissait l'onglet, il semble que, dès la seconde moitié du 15^e siècle, l'onglet ait participé à la conception générale de la perspective. Dans un certain nombre de cadres présentant une coupe droite, un onglet est peint. La ligne de l'onglet correspondait parfaitement aux lignes mises en perspective par le peintre qui conduisaient le regard vers le centre du tableau. L'onglet, peint ou réel, a participé de même que la mouluration et la polychromie du cadre, à la conception illusionniste de l'art flamand du 15^e siècle. Le débordement de la composition peinte sur la traverse inférieure en talus est un autre aspect de cette conception.

La forme des grands retables

Nous avons étudié ailleurs les transformations subies au cours des temps par les cadres et supports de l'*Agneau mystique* de van Eyck (4) mettant l'accent sur l'incidence que le poids des volets du registre supérieur a eu sur l'ouverture et la fermeture de l'oeuvre selon les besoins, amenant à raccourcir les volets dans le haut pour en diminuer le frottement. A la suite d'une étude attentive de l'oeuvre à l'occasion de son déménagement en 1986 - nous avons pu proposer une reconstitution de son état primitif montrant que les volets recouvraient complètement la surface de la partie dormante (fig. 4.a).

Les grands retables de forme rectangulaire, comme l'était le registre inférieur du polyptyque de l'*Agneau mystique*, n'ont pas posé de problèmes particuliers. Ils ont continué à être en usage au cours des 15^e et 16^e siècles. Dans d'autres cas, le programme iconographique entraînait la nécessité d'une partie centrale surélevée, comme dans le registre supérieur du polyptyque. Vers 1438, Roger van der Weyden peint la *Descente de croix* du Prado. Par ailleurs, comme dit plus haut, le revers du panneau conservé à Madrid présente des traces de l'existence à l'origine d'un châssis fixé au cadre original, construction aujourd'hui disparue, mais qui ne s'explique, pensons-nous, que pour résister à la charge des volets. Le centre surélevé du retable est fortement rétréci (59 cm) par rapport à celui de l'oeuvre de van Eyck (82 cm). Au détriment des proportions, mais pour assurer la bonne construction, cette réduction permettait de limiter la partie exhaussée des volets (fig. 4.b).

Vers 1446-1448 van der Weyden réalise le *Polyptyque du Jugement dernier* de Beaune (fig. 4.c). La couverture de la partie centrale surélevée est assurée par deux petits volets qui lui sont directement attachés et s'articulent donc à la partie centrale, permettant un allègement considérable des grands volets et un retour à de meilleures proportions de la partie exhaussée (112 cm). Cette solution sera souvent adoptée à la fin du 15^e siècle.

On peut inscrire à la suite de cette évolution la forme chantournée qui apparaît au début du 16^e siècle. A une meilleure répartition des charges, cette

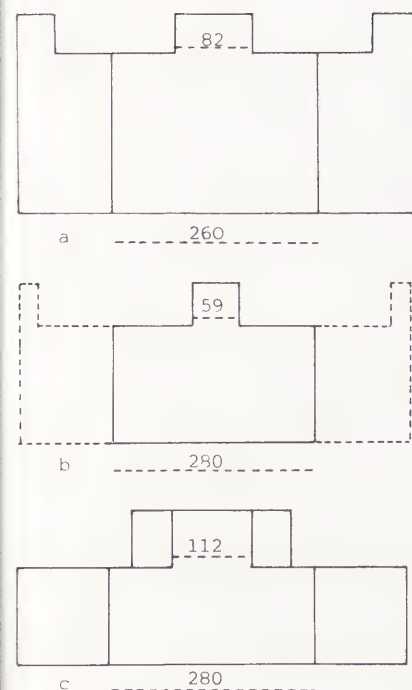


fig. 4.a : van Eyck, *Agneau mystique*, Gand, Saint-Bavon, schéma du registre supérieur (reconstitution). b : van der Weyden, *Descente de croix*, Madrid, Prado, schéma (reconstitution). c : van der Weyden, *Polyptyque du Jugement dernier*, Beaune, Hospices, schéma

forme joignait l'avantage de permettre la construction de la traverse supérieure des volets en une seule pièce, lui donnant donc une meilleure solidité et plus d'élégance.

Références

- (1) P.J.J. Van Thiel et C.J. De Bruyn Kops, *Prijst de Lijst. De Hollandse schilderijlijst in de zeventiende eeuw*, Den Haag, 1984.
- (2) H. Verougstraete-Marcq et R. Van Schoute, *Cadres et supports dans la peinture flamande aux 15e et 16e siècles*, Heure-le-Romain, 1989.
- (3) J.R.J. Van Asperen de Boer, R. Van Schoute, M.C. Garrido et J.M. Cabrera, *Algunas cuestiones tecnicas del Descendimiento de la Cruz de Roger van der Weyden*, dans *Boletin del Museo del Prado* (IV) 10, 1983, p. 39-50.
- (4) H. Verougstraete-Marcq et R. Van Schoute, *Les cadres de l'Agneau mystique de van Eyck*, dans *Revue de l'Art*, 77, 1987, p. 73-76.

ABSTRACT

During research on early 17th c Flemish panel paintings the personal marks of several panel makers have been recorded stamped into the wood. However, also marks written with a piece of red chalk have been found. They are hard to trace in normal light but by means of a UV-lamp the written marks become easier to read. Documentation of marks written with a red chalk crayon may be stored on UV-fluorescence photographs.

KEYWORDS

17th century, panel painting, Antwerp, panel makers marks, red chalk, UV-fluorescence, documentation, matrices.

17th c FLEMISH PANEL MAKERS' RED CHALK MASTER MARKS.

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Introduction

At the end of the 15th c the guild of St. Lukas in Antwerp introduced a quality control on the wooden objects made by the carpenters. Approved works of art carved in oak were stamped, or branded, with the city arms of Antwerp: the two hands and the three towers of the city wall¹.

On panel paintings from the early 17th c the city arms of Antwerp are stamped with one matrice. Next to this mark, with another matrice, the panel makers' personal mark may be found. Most often these personal marks are depicting the monogram of the panel maker, e.g. that of Michiel Vriendt: "MV", Nicholas Vriendt: "NV", Lambrecht Steens: "LS" and "G+G" for Guilliam Gabron². Apart from monograms also symbols were used such as the clover leaf by the panel maker Michiel Claessens and a cross over a circle used by Hans van Herentals³.

During research on 75 flemish panel paintings placed in their original setting in Rosenborg Castle in Copenhagen, Denmark, several marks were found on the back of 30 of the panels⁴. The clover leaf of Michiel Claessens is seen on 4 panels and a six-pointed star, the mark of a still unidentified panel maker working after 1619⁵, is found once. All of them are stamped into the wood.

Written marks

However, two panel makers have applied their personal mark on the back of the oak panels using a piece of red chalk⁶: a circle with a X-across "X" and a monogram "A". The first mark was found only once in the Rosenborg Collection and is the mark used by Hans van Herentals. The other mark, the monogram, has been found on 8 panels, and is the mark of Guilliam Aertssens⁷.



Fig. 1: Back of panel painting viewed in normal light. South wall no. 10 in Winter Room, Rosenborg Castle, Copenhagen.

The writings with red chalk are very difficult to read, as very often only little of the porous material is left on the rough wood surface. They may therefore often have passed even a trained conservator's eye without being noticed.

UV-fluorescence examination

Examining the panel's backs with a UV-lamp, however, makes the red chalk turn dark as it absorbs the ultraviolet light waves. The oak panel on the contrary almost keeps its light tone, thus enhancing the contrast between the red chalk and the panel: the marks are easier to trace. They can be recorded using UV-fluorescence photography (b/w or colour).

The paintings in Rosenberg Castle are in their original frames and on 13 of these the red monogram of Aertssens have been traced. Frames and panels have been fitted together in Antwerp before being exported to Denmark, and in order not to make any mistake when placing the panel in its companion frame, both have been marked with numbers. These numbers, also written with the red chalk crayon were too documented using UV-fluorescence light.

Written marks: a normal practice

Being doubtful whether the marks made with the red chalk crayon were found only in connection with the panels in Rosenberg Castle I have examined all the Flemish panel paintings on exhibition and in the stores of a series of French museums and art galleries⁸.

Marks stamped into the wood were found at all the places visited and on two occasions the mark written with the red chalk crayon by Guiliam Aertssens were discovered: on the back of a painting by Adriaen van Stalbemt⁹ and on one by Joos de Momper¹⁰.

It then seems proved that written panel makers marks, as marks stamped into the wood with matrices, were used at the same time. The Momper painting mentioned above actually also had Aertssens' stamped mark placed next to the mark written with red chalk.

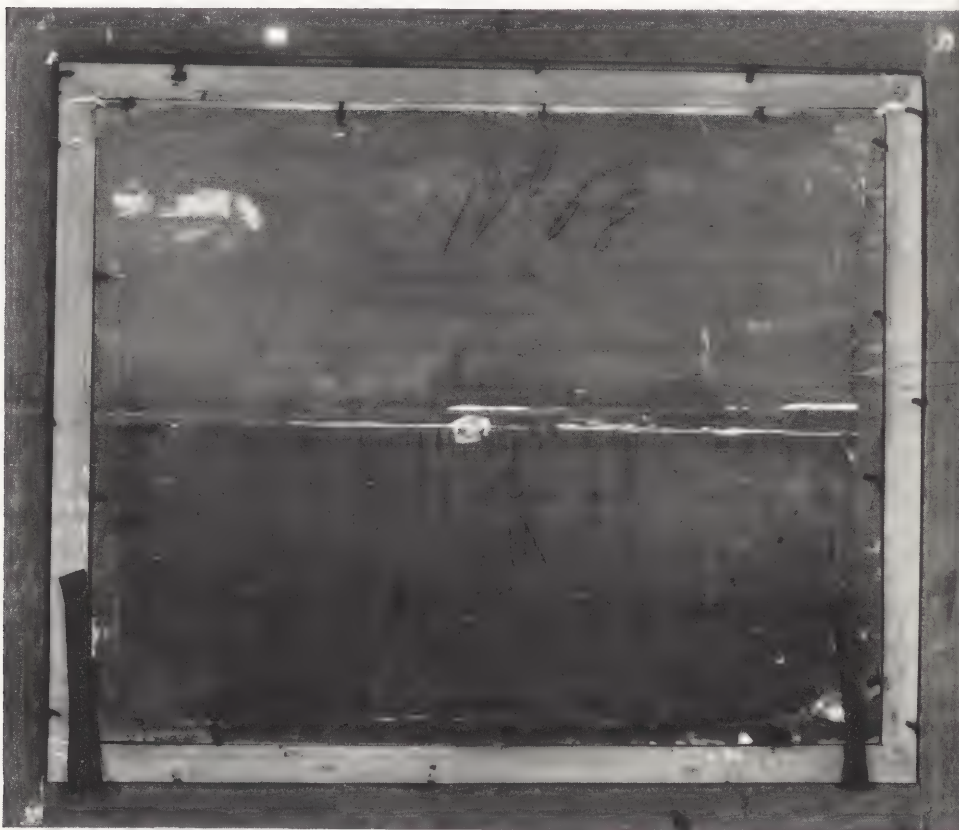


Fig. 2: Back of the same panel as in fig. 1 photographed in UV-fluorescence light. The writings in red chalk are now readable: "N° 68" and the "A"-monogram of the panel maker Guiliam Aertssens. In the middle of the left piece of the frame a part of the makers' mark also is to be seen. The bright line in the middle is the fluorescence from the glue used by Aertssens when he in ± 1618 glued the two pieces of wood together forming the panel.

Conclusion

In order to trace panel makers personal marks written with red chalk on the back of Flemish panel paintings from the 17th century UV-fluorescence examinations of the back of paintings are strongly recommended.

A lasting documentation of the written marks on the back of panels may be stored well on black & white (and colour) photographs made in UV-fluorescence light.

Acknowledgements

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Notes

- 1: J. Bosschère: *La sculpture anversoise aux XV^e et XVI^e siècle*, Bruxelles 1909.
- 2: G. Gepts: *Tafereelmaker Michiel Vriendt, leveranciers van Rubens*, *Jaarboek Koninklijk Museum voor Schone Kunsten Antwerpen* 1954-60.
- : H. von Sonnenburg: *Rubens' Bildaufbau und Technik*; *Maltechnik-Restauro* 2, 1979.
- 3: J. Van Damme: *De Antwerpse "tafereelmakers" en hun merken*; *De Leiegou*, Jg. XXIX, afl. 1-2, Kortrijk 1987.
- 4: J. Wadum: *The Winter Room at Rosenborg Castle; A Unique Survival of Antwerp Mass-Production*; *Apollo* vol. CXXVIII, no. 318, London August 1988.
- 5: Recently the author discovered a small panel with the six-pointed star on the back. The painting was indistinctly signed with a monogram and the year "1619"; attr. to Dirk Hals. Arne Bruun Rasmussen, Auctioneer of Fine Art, Copenhagen.
- 6: The marks were tested in situ with a weakly acid solution of potassium ferrocyanide under the stereo microscope. The formation of a blue colouration confirmed the presence of Fe(III) indicating ironoxide, typical for red chalk. No further characterization of the material was attempted.
- 7: J. Van Damme: *ibid*.
- 8: The museums examined are: Musée des beaux-Arts in Dijon, Musée des Beaux-Arts in Lille, Musée de la Chartreuse in Douai, Musée des Beaux-Arts in Valenciennes and Galerie J.O. Leegenhoek, Galerie Gismondi, Galerie de Jonckheere, Galerie Jean-Max Tassel all in Paris.
- 9: Adriaen van Stalbeem (1580-Antwerp-1662): *The Flight into Egypt*, panel 54,5 cm x 76,0 cm. Musée des Beaux-Arts in Dijon, inv.no. J.69.
- 10: Joos de Momper II (1564-Antwerp-1635): *Mountain Landscape*, panel 49,0 cm x 80,5 cm. Galerie Jean-Max Tassel, Paris.

Bibliography

- A. Heppner: *Ingebrande Merkteekenen ("Brandmarken") en hun waarde voor de kennis van Schilderijen*; *Oud Holland*, Jg. LVIII, afl. 1-6 Amsterdam 1940.
- G. Gepts: *Tafereelmaker Michiel Vriendt, leverancier van Rubens*; *Jaarboek voor het Koninklijk Museum voor Schone Kunsten Antwerp* 1954-60.
- H. von Sonnenburg: *Rubens' Bildaufbau und Technik*; *Maltechnik-Restauro* 2, München 1979.
- R.H. Marijnissen: *Schilderijen. Echt-fraude-vald. Moderne onderzoekingsmethoden van de schilderijenexpertise*; Brussel-Amsterdam 1985.
- J. Van Damme: *De Antwerpse "tafereelmakers" en hun merken*; *De Leiegou*, Jg. XXIX, afl. 1-2, Kortrijk 1987.
- B. Cardon: *Antekeningen bij de Annunciatie uit het voormalige cellebroedersklooster te Dienst, thans in het Stedelijke Museum aldaar; Arca lovaniensis artes atque historiae reserans documenta*, *Jaarboek* 15-16, Leuven 1987.
- J. Wadum: *The Winter Room at Rosenborg Castle; A Unique Survival of Antwerp Mass-Production*; *Apollo* vol. CXXVIII, no. 318, London August 1988.



Fig. 3: Detail of fig. 2 showing the personal mark of Guiliam Aertssens.



Fig. 4: Rubbing of the city arms of Antwerp and the personal mark of Aertssens. Both are stamped with matrices into the back of the panel.

- J. Wadum: Mestermærker på Flamske 1600-tals tavlemalerier; Meddelelser om Konservering 3.hefte, 4.række, 1989 (engl. summary).
- M. Schuster-Gawlowska: Remarques de restaurateur sur les marques apposées sur les supports de bois des tableaux flamands; Traitement des supports travaux interdisciplinaires, 2-4 Novembre, Paris 1989.
- M. Schuster-Gawlowska: Marques de corporations, poinçons d'ateliers et autres marques apposées sur les supports de bois des tableaux et des retables sculptés flamands. Essai de documentation à partir des collections polonaises; Jaarboek voor het Koninklijk Museum voor Schone Kunsten Antwerp 1989.



Fig. 5: Back of panel in normal light.



Fig. 6: Same as above but in UV-light. The maker's mark is recorded

Working Group 20

Glass, Ceramics and Related Materials

Verres, céramiques et matériaux
apparentés



ABSTRACT

Hxtal NYL-1 an epoxy and Loctite 350 an acrylic adhesive have been evaluated for use in the conservation of glass, particularly the Portland Vase at The British Museum. The results of accelerated ageing of the adhesives using light and heat ageing regimes are reported. Hxtal NYL-1 was found to have good colour stability to light ageing but poor stability to heat ageing. It is reversible using solvents. The colour stability of pigmented samples of Hxtal resin was also investigated. Preparation of pigmented resin was found to be difficult, and the colours investigated exhibited some fading during light ageing. Loctite 350 was found to yellow slightly during both light and heat ageing and to be reversible using solvents followed by mechanical removal.

EVALUATION OF HXTAL NYL-1 AND LOCTITE 350 ADHESIVES FOR GLASS CONSERVATION

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INTRODUCTION

During 1981 and 1982 several epoxy and polyester resins were evaluated for use in the conservation of glass at The British Museum. The results of the accelerated ageing tests carried out at that time showed that exposure to heat at 70°C for 28 days caused greater yellowing of samples than exposure to an intense daylight spectrum lamp for 2000h. Since the results of the tests were reported (1) the samples have been exposed on a wall in the author's laboratory and subject to the normal daily cycle of natural daylight, artificial light and night time. In the intervening seven years the heat aged samples which were yellowed have remained unchanged indicating that the resins yellow to a finite extent, the light aged samples have darkened to an extent similar to the heat aged samples, and the control samples have yellowed to an extent which is intermediate between the initial colours of the light and heat aged samples. These results have led the author to conclude that the results of heat ageing must be considered together with the results of light ageing when evaluating the colour stability of resins using accelerated ageing tests. Although natural ageing may be a superior method of assessment (2) time considerations favour accelerated ageing tests.

Hxtal NYL-1 epoxy and Loctite 350 acrylic adhesives have been evaluated for general use in the conservation of glass in The British Museum and specifically for use in the conservation of the Portland Vase. Accelerated heat and light ageing regimes have been used to assess the stability of Hxtal NYL-1 a two component epoxy adhesive and Loctite 350 a light curing acrylic adhesive. Hxtal NYL-1 was introduced into conservation during 1982-83 by Mr H Hillary (4). It was reported to be a low viscosity, colourless, colour stable adhesive suitable for use as an adhesive for glass. The resin was described as an hydrogenated epoxy resin and the hardener as a polyoxypropylene triamine hardener with imidazole accelerator (5). Curing time was reported to be 20h to 7 days at ambient temperature.

Loctite 350, a light curing acrylic adhesive was developed for use with glass and introduced into conservation about two years ago. The one component, medium viscosity, modified methacrylic ester adhesive (6) is cured by ultraviolet light. A join has to be perfectly aligned before the light source is directed along it as the adhesive cures within seconds.

The effects of light and heat ageing on ease of reversibility and colour stability were determined. Fourier transform infrared spectroscopy was used to investigate two batches of Hxtal NYL-1 supplied by Mr Hillary and the effect of ageing on the cured adhesive. The adhesives were also evaluated for use in the conservation of the Portland Vase (7) and for this purpose the effect of ageing on pigmented samples of Hxtal NYL-1 was determined. The tensile strength of joins prepared with both adhesives was investigated.

EXPERIMENTAL**Sample Preparation**

Samples were prepared on microscope slides which had been degreased with acetone. The adhesives were spread onto the slides to form thin films and allowed to cure.

Hxtal NYL-1

Two batches of Hxtal NYL-1 were received. Batch I was mixed 4:1, resin:hardener. Batch, II was said to have been improved by charcoal filtration of both the resin and hardener to improve the colour, and reaction of the resin with sodium borohydride. The latter presumably being to reduce any aldehydes, and ketone groups present to alcohol groups. This batch was mixed in the stoichiometric ratio of 3:1, resin:hardener (5).

Batch I of the Hxtal adhesive was often used pre-accelerated by the conservators. The resin was pre-accelerated by heating it above a beaker of boiling water for 15 minutes stirring occasionally. The effect of this heating was to speed up the rate of curing to approximately 24h. Therefore two sets of samples were prepared, one by mixing the two components as supplied, the other by mixing pre-accelerated resin with hardener. Batch II of the Hxtal adhesive was used as supplied only following discussions with Mr Hillary (5) who suggested that curing at 43°C after mixing the resin would result in a curing time of 24 hours or less.

Pigmented Hxtal NYL-1

Two methods of preparing transparent coloured fills in coloured glass were considered. These were making the fill from clear resin and painting the external surface of the fill with a pigmented lacquer, or adding pigment to the resin so that the fill would be coloured throughout. The latter approach was thought to be more suitable for use with a highly coloured glass.

A deep cobalt blue was needed and pigments currently in use in the Ceramics and Glass Section were selected for mixing into the Hxtal NYL-1 resin to prepare a suitably coloured resin. Mixing the colours into the resin was difficult, and it became apparent that the pigments would not disperse using any of the stirring facilities available to the section. The reason for this was diagnosed as the viscosity of the resin being too low to cut and disperse the pigment.

Mr Hillary produced three pigmented samples of resin using Phthalocyanine blue, Keyplast blue BGP and Key oxazine violet prepared by mixing in a high speed blender or a ballmill for up to 24h, using clear Hxtal NYL-1 Batch II which had been heated to 49°C. All the samples were optically dense and the cobalt blue colour required was finally obtained by mixing Hxtal containing Keyplast blue BGP and Keyoxazine violet with clear hxtal prior to mixing the resin with the hardener. Samples of the different colours were prepared by painting mixed resin and hardener onto microscope slides degreased with acetone. Pooling on the slides occurred which was prevented by degreasing with soap and water.

Loctite 350

Loctite 350 adhesive was spread on microscopic slides to form a thin film and exposed to a Flexiarc type UVLS101 lamp for 90 seconds. The surface of the adhesive did not fully cure. Silicone release paper was pressed against the partially cured surface before exposing the samples to the light source for a further 15 seconds. This resulted in full curing of the samples.

Joins

Test joins were prepared using Hxtal NYL-1 and Loctite 350 in microscope slides which had been cut in half with a glass cutter. The edges of the microscope slides were degreased using acetone prior to application of the adhesive. Hxtal NYL-1 Batch I was used pre-accelerated and as supplied.

Accelerated ageing regimes

Heat ageing was carried out to simulate ageing in the dark, the samples being placed in an oven at 70°C for 28 days. Light ageing was carried out in a Microscal Light Fastness tester with a daylight spectrum lamp and was continued until the samples showed signs of yellowing when examined visually.

Evaluation tests

Reversibility

The reversibility of the samples was assessed qualitatively before and after ageing by immersing fragments of coated microscope slides in acetone, toluene, dichloromethane and tetrahydrofuran in sealed sample tubes for 24h. Since neither Hxtal or Loctite adhesive dissolved in the solvents the reversibility was assessed by the extent to which the adhesive was separated from the glass.

Colour

The colour of the samples before and after ageing was determined by measuring their UV-visible reflectance spectrum samples in a Perkin Elmer 551S UV-visible spectrophotometer fitted with an integrating sphere. The CIE L^* a^* b^* coordinates, and hence colour change (ΔE), were calculated from the spectra. ΔE was calculated using equation 1

$$\Delta E = [(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2]^{1/2} \quad (1)$$

Where L_1^* , a_1^* and b_1^* are coordinates for the control sample

and L_2^* , a_2^* and b_2^* are coordinates for the aged sample.

Fourier Transform Infrared spectra

The Fourier transform infra red (FT-IR) spectrum of the Hxtal NYL-1 adhesives were obtained using a Perkin Elmer Model 1700 Fourier Transform Infra Red Spectrometer. The FT-IR spectrum of the uncured Hxtal resin and hardener and cured control, light aged and heat aged samples were obtained between 4000 and 400 cm^{-1} . The spectra were used to observe differences in the chemistry of the two batches of Hxtal NYL-1 adhesive and differences resulting from ageing of the adhesives.

Strength

The tensile strength of the joins was measured using a JJ Lloyd model 15003 bench top tensile testing machine. The tensile strength of the join was calculated using equation 2.

$$\text{Tensile strength} = \frac{\text{Force Nm}^2}{\text{area}} \quad (2)$$

The variability coefficient of the measurements was calculated.

RESULTS

Clear Hxtal NYL-1 adhesive

Reversibility

The results of the reversibility tests on batch I of the adhesive are shown in Table I. The tests were not repeated for batch II of the adhesive.

Sample	Solvent			
	Acetone	Toluene	Dichloromethane	Tetrahydrofuran
Control	Disruption	Disruption	Separation	Separation
Light aged	No effect	Slight disruption	Separation	Separation
Heat aged	No effect	No effect	Separation	Separation

TABLE I

The adhesion of Hxtal NYL-1 to glass was found to be reversible in dichloromethane and tetrahydrofuran both before and after ageing.

Colour

The colour stability of batch I and II of Hxtal NYL-1 to ageing was determined. The UV visible spectra for all samples of Hxtal NYL-1 batch I are shown in Figure 1. The curves and the visual assessment indicate that only very slight yellowing of the adhesive occurred when exposed in the light fastness tester for 2000h. Severe yellowing occurred to the heat aged samples which were then exposed in the light fastness tester to determine whether yellowing was reversible by bleaching. Typical curves obtained for reversion of the effects of heat ageing on Hxtal NYL-1 batch I are also shown in Figure 1.

The CIE L^* a^* b^* coordinates calculated from the curves and the colour change ΔE are shown in Table II.

Sample	CIE			ΔE
	L*	a*	b*	
HXTAL NYL-1 Batch I				
Control	90.287	-0.483	1.096	
light aged	90.530	-0.4880	1.039	0.249
heat aged	88.732	-4.742	13.041	12.775
& exposed to light 361h	89.613	-2.744	6.989	6.348
& exposed to light 4561h	90.471	-1.054	3.230	2.209
HXTAL NYL-I Batch 1				
PRE ACCELERATED				
Control	90.761	-0.510	1.061	
light aged	91.211	-0.722	1.471	0.644
heat aged	88.440	-5.720	17.297	17.208
& exposed to light 361h	87.713	-1.923	4.374	4.719
HXTAL NYL-1 Batch II				
Control	93.435	-0.288	0.631	
light aged	94.097	0.165	0.798	0.869
Control	93.331	-0.1556	0.471	
heat aged	91.990	-3.296	7.627	7.929

TABLE II

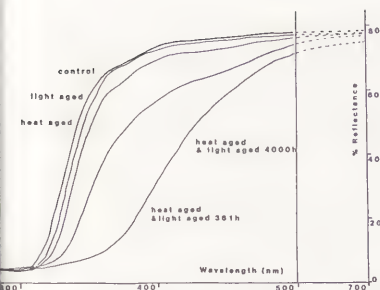


Figure 1 UV-visible spectra of batch I Hxtal samples

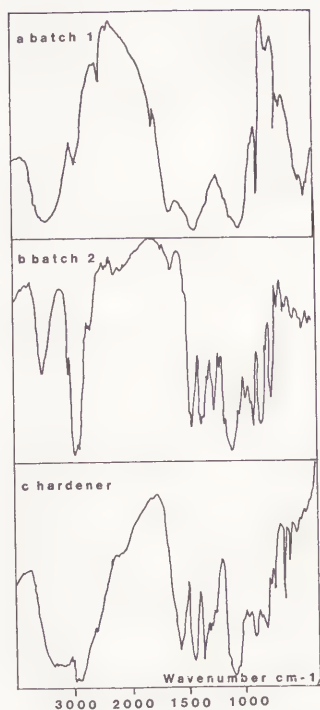


Figure 2 FT-IR spectra of Hxtal NYL-1 resins & hardener

The slight yellowing of Hxtal NYL-1 after 2000h of light ageing compares favourably with other epoxy systems (1) and is similar to results we have obtained for the yellowing of Paraloid B72 in the light fastness tester. Both batches of Hxtal yellowed during heat ageing, but this was less pronounced for batch II. Pre-accelerating batch I caused the Hxtal to yellow to a greater extent during both light and heat ageing. Exposing the batch I heat aged samples in the light fastness tester resulted in some reversal of the yellowing caused by heat ageing. The spectra of these samples were measured several times between 361 and 4561h exposure. Maximum reversal was obtained at 4000h exposure and further exposure to 4561h did not increase the extent of reversal. These results suggest that exposure of the adhesive to normal daily cycles of light and dark will result in some yellowing. Comparison with the results of previous ageing tests on epoxy resins discussed in the introduction suggest that the Hxtal NYL-1 adhesive is likely to yellow to a colour between that indicated by light ageing and that indicated by heat ageing.

Fourier Transform Infra-Red Spectra

Comparison of the spectra obtained for the batch I and batch II resins suggested that there were considerable differences between the two, see Figure 2a and b. It is not clear whether this was as a result of filtration and reaction of the batch II resin with sodium borohydride. The spectra of the hardener for both batches was identical, Figure 2c. The spectra of cured samples of batch I and pre-accelerated batch I were identical, Figure 3a, as were those of the heat and light aged samples, Figures 3b and 3c. A change in the structure observed following heat and light ageing occurred in the region 1550-1720 cm^{-1} . Two peaks, 1600 and 1720 cm^{-1} were present in both control samples. The four heat aged and light aged samples exhibited peaks at 1720, 1640, 1600 and 1550 cm^{-1} . No substantial change was observed in any other part of the spectrum. The similarity in the spectra of the aged samples suggested that the results of the light and heat activated reactions were similar, although considerably more yellowing was apparent as a result of heat ageing. This was presumably caused by formation and conjugation of double bonds in the structure.

Pigmented Hxtal NYL-1 adhesive

Colour

The colour stability of the samples on light and heat ageing was determined. Light ageing was carried out for 1000h and heat ageing for 28 days at 70°C. The results of L^* a^* b^* and ΔE calculations are given in Table III.

Sample		L^*	CIE a^*	b^*	ΔE
Phthalocyanine blue	- control	65.108	-34.807	-35.407	
	- light aged	67.425	-32.710	-33.850	3.451
	- heat aged	59.429	-43.934	7.769	44.978
Keyplast blue	- control	46.029	8.464	-70.725	
	- light aged	67.830	-15.213	-36.352	47.089
	- heat aged	45.734	-9.595	-39.461	36.106
Keyoxaxine violet	- control	17.017	25.256	-32.964	
	- light aged	19.246	61.589	-66.458	49.452
	- heat aged	24.860	40.025	-46.693	21.636
Keyblue violet:	- control	27.081	44.883	-64.106	
clear hxtal	- light aged	16.922	40.085	-54.279	14.926
1:1:2	- heat aged	42.056	23.388	-57.977	26.904

TABLE III

The results show that the pigmented resin samples fade on exposure to light. The Keyplast blue and Keyoxaxine violet appear to be more stable to heat ageing than to light ageing.

Loctite 350 Adhesive

Reversibility

The reversibility of the adhesive was assessed qualitatively as described above and the results are given in Table VI.

Sample	Acetone	Toluene	Solvent Dichloromethane	Tetrahydrofuran
Control	Softened	Softened and flaked	Swelled	Swelled with disruption
Light aged	Softened	Flaking	Disruption	Disruption
Heat aged	Softened	Flaking	Disruption	Disruption

TABLE IV

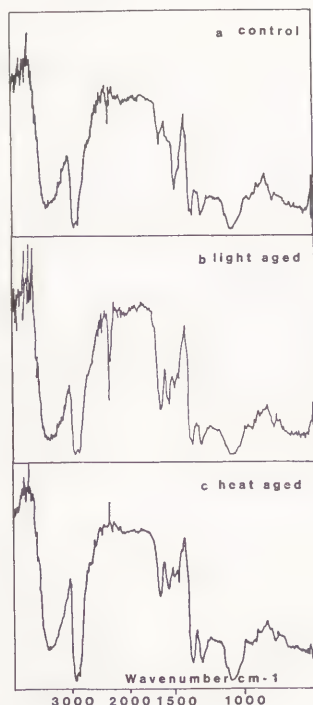


Figure 3 FT-IR spectra of cured control and aged Hxtal NYL-1 samples

Colour

The colour stability of Loctite 350 adhesive to heat and light ageing was determined. A visual assessment of the aged samples indicated that some yellowing had occurred during both heat and light ageing. The UV-visible spectra of the samples were used to calculate CIE L^* a^* b^* coordinates and hence colour change from the control sample ΔE . The results are given in Table V.

Sample ΔE	
Light aged	5.572
Heat aged	6.601

TABLE V

These results indicate that light and heat ageing cause yellowing to a similar extent.

Joins

Prepared joins were exposed in the light fastness tester for 2000h and heat aged for 28 days at 70°C.

Colour

The colour of the joins was assessed visually by comparison with control samples. None of the joins showed signs of yellowing.

Tensile Strength

The results obtained for the unaged joins are given in Table VI.

Sample	Tensile strength Nm^{-2}		Variability Coefficient
	Mean	Range	
Hxtal NYL-1	7.0	3.5 - 9.8	13.2
Hxtal NYL-1 (pre-accelerated)	20.2	17.6 - 24.0	23.0
Loctite 350	28	26 - 33	15.7

TABLE VI

The number of samples measured was small, being six in each group. The variability of the results indicated that many more samples would need to be tested to give significant tensile strength values. However the general trend of the results is that Loctite 350 adhesive gives a stronger bond in clear glass than Hxtal NYL-1.

The measurements made on aged joins were highly variable and did not indicate any trend towards reduction or increase in adhesion.

Discussion

The results of the tests suggest that Hxtal NYL-1 is a light stable adhesive, but in common with other epoxy adhesives is subject to yellowing when heat aged. The results of bond strength tests were too variable to indicate either an increase or decrease in bond strength on ageing. The ageing of pigmented samples of Hxtal NYL-1 suggested that some colour change may occur under normal display conditions in a museum. In reversibility tests Hxtal NYL-1 was more readily separated from glass than was Loctite 350, although removal could be achieved by a combination of softening in solvent followed by mechanical removal.

Loctite 350 adhesive yellowed in both light ageing and heat ageing suggesting that yellowing will occur during the lifetime of the adhesive on an artefact (50-100 years). However the handling properties of Loctite 350 and the bond strength achieved in clear glass were superior to those of Hxtal NYL-1. The results of tests on both adhesives indicate that they are useful materials to be added to the repertoire of glass conservators.

Taking into account all of the observations the procedure chosen for repair of the Portland Vase was to first tack the joins using spots of Loctite 350 cured with a UV light source. This allowed the vase to be constructed in sections and the alignment of joins to be checked before they were finally adhered using Hxtal NYL-1 (batch I). Joins which were incorrectly aligned were reversed by using dichloromethane to soften the Loctite adhesive. This process was easier than predicted from experimental work, perhaps suggesting that the blue glass of the vase affected the cure of the adhesive. Gaps in the fabric of the vase were filled using pigmented Hxtal NYL-1 (batch II). An appropriate colour was achieved using a mixture of Keyplast blue, Key Oxaxine violet and clear Hxtal. The vase has now been returned to exhibition in The British Museum where the effects of the conservation can be seen (7).

References

- (1) Bradley, S.M., and Wilthew, S.E., The evaluation of some polyester and epoxy resins used in the conservation of glass, in Preprints of ICOM Committee for Conservation, 7th Triennial meeting, Copenhagen, 1984 (1984).
- (2) Down, J.L., Adhesive testing at the Canadian Commonwealth Institute, past and future in Adhesives and Consolidant Preprints of the contributions to The Paris Congress, 2-8 September 1984, IIC, London (1984) 18-21.
- (3) Personal Communication Miss K Norman, then a conservator in the Ceramics and Glass Section, British Museum.
- (4) Williston, S.S., Epoxy Hxtal NYL-1, AIC Newsletter, Vol 8, No 2, (1983) 14.
- (5) Personal Communication from Mr H Hillary, 1909 Richcreek Rd, Austin, Texas 78757.
- (6) Loctite Products, Technical Information 350, Loctite UK Ltd, Loctite Holdings, Watchmead, Welwyn Garden City, Herts AL7 1JB, UK.
- (7) Williams, N., The Breaking and Remaking of The Portland Vase, RM Publications Ltd, London (1989)

Material Suppliers

Pigments, Keystone Aniline Corporation of Chicago, USA.

Loctite 350, Loctite UK, Loctite Holdings Ltd, Watchmead, Welwyn Garden City Herts AL7 1JB.

Hxtal NYL-1, Mr H Hillary, 1909 Richcreek Rd, Austin, Texas 78757, USA.

Health and Safety

Adhesives

Protective clothing, gloves and goggles should be worn when handling Hxtal resin and hardener and Loctite 350 since they can all cause severe irritation especially on areas of bruised or cut skin. If skin contact occurs the resin and hardener should be removed by wiping with disposable paper towels and the skin washed in soapy water. If eye contact occurs irrigate with low pressure running water for at least fifteen minutes and seek medical attention.

UV light source

To prevent exposure of the skin on the hands to the UV light source used for curing protective gloves should be worn when aligning and curing joins. UV goggles should be worn when using the light source.

Acknowledgements

I would like to acknowledge the help of Mrs Sandra Smith who prepared the resin samples, Mr Jinping Zhang who calculated the CIE co-ordinates and colour changes and Mr H Hillery and Mr N Williams for discussions on the conservation of the Portland Vase

ABSTRACT

Twelve efflorescence salt samples from archaeological ceramics stored in wooden cabinets were analyzed by Neutron Activation Analysis and eight of these samples were also analyzed by X-ray Diffraction. The scope of the analysis was to determine the identity of these salts and the requirements for their formation. The relative humidity of the storage area was monitored for the period of one year. Calclacite, calcium acetate chloride pentahydrate ($\text{Ca}(\text{CH}_3\text{COO})\text{Cl} \cdot 5\text{H}_2\text{O}$), was identified as the major phase in two of the samples and as a minor phase in several of the others. Further investigation will comprise the analysis of numerous efflorescent salts as well as the host ceramic fabric from the ancient Agora collection by Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD).

KEYWORDS

Salt, efflorescence, ceramic, pottery, archaeological, Athens, Agora, Greece, analysis, X-ray Diffraction, Neutron Activation Analysis, storage, relative humidity, organic vapours, wood, calclacite, conservation

A PRELIMINARY STUDY OF SALT EFFLORESCENCE IN THE COLLECTION OF THE ANCIENT AGORA, ATHENS, GREECE

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Introduction

The prevalence of efflorescence on ceramic objects in the Agora collection has instigated the investigation of these salts to determine:

- 1) the identity of these salts,
- 2) the cause(s) of their formation,
- 3) the influence of environmental relative humidity (RH) on their formation,
- 4) the influence of storage materials and conditions on their formation, and
- 5) the role fabric composition and porosity may play on the formation of efflorescence.

A survey was made during two consecutive summers of one storage area in the study collection of the Agora which contains hundreds of small ceramic objects and sherds stored in wooden drawers within wooden cabinets. The cabinets and drawer sides are constructed of coniferous wood and the bottom of the drawers are plywood. These cabinets were constructed sometime between the 1930's and the 1950's. Every object displaying efflorescence was noted and the salt formations were described as 1) powder-like, 2) needle-like, or 3) snowflake pattern.

The relative humidity was monitored in this storage room for a period of one year taking two measurements daily (7:30 A.M. and 2:30 P.M.) with a hair hygrometer. The monthly highs and lows and the maximum daily fluctuation each month are presented in Graphs 1 and 2. The changes in RH inside the drawers can be expected to be slower than those recorded. It was noted that formations of efflorescence are much more evident and in greater abundance during the summer when the relative humidity is lowest.

In order to carry out this investigation 12 efflorescence samples were analyzed by Neutron Activation Analysis and 8 of these samples were also analyzed by X-ray Diffraction. A description of the samples and host objects reveals that each of the three salt morphologies is represented as is a wide range in date of object, provenance, date of excavation, and shape and function (Table 1). Other variable factors include fabric type, firing temperature, and burial conditions. Conservation treatment records were not made systematically in the Agora prior to 1979 and, based on verbal communication with those involved with the excavation for many years preceding 1979, it is known that much of the pottery was washed in hydrochloric acid. The method of application of the acid and concentration used is left to the imagination.

Table 1

Sample No.	Salt* Morph.	Glaze	Date of Execution	Date of Excavation	Object Description	Inv. No.
1	n.l.	yes	1st c. B.C.	1934	Pergamene plate	P3785
2	n.l.	yes	5th c. B.C.	1936	Greece lamp	L2658
3	n.l.	no	4th c. A.D.	1947	Roman lamp	L4189
4	n.l.	yes	4th c. B.C.	1947	Greek skyphos	P18420
5	n.l.	yes	1st c. A.D.	1948	Greek lamp	L4464
6	n.l.	yes	5th c. B.C.	1936	Greek public measure	P8098
7	n.l.	yes	3rd c. B.C.	1957	Greek lamp	L5312
8	n.l.	no	3rd c. A.D.	1947	Roman lamp	L4518
9	s.f.	wash	4th c. A.D.	1933	Roman lamp	L1060
10	s.f.	no	4th c. A.D.	1936	Roman lamp	L1993
11	s.f.	no	5th c. A.D.	1934	Roman lamp	L1329
12	p.l.	yes	3rd c. B.C.	1951	Greek lamp	L4836

* n.l. = needle-like, p.l. = powder-like, s.f. = snowflake pattern

Analytical Procedures

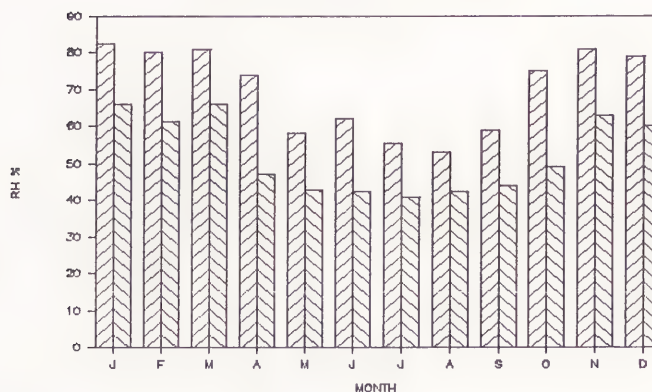
Neutron Activation Analysis

The samples were irradiated using the Slowpoke ⁻² nuclear reactor at the Royal Military College, Kingston, Ontario, Canada, for one minute with a flux of $5 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$. There was a 10 minute delay before counting due to the high gamma energy levels from aluminum. The resulting gamma radiation was measured using a high purity germanium detector and a Nuclear Data multichannel analyzer, and the data collected used for the determination of aluminum, chlorine, magnesium, manganese, sodium, vanadium, titanium and calcium. By bombarding the sample with slow neutrons in a nuclear reactor some of the atomic nuclei capture a neutron and some of these new isotopes are radioactive. As these radioactive isotopes decay, some emit gamma rays whose energies are characteristic of the particular element. The qualitative determination of the element present in the sample is based on the energy of the gamma rays and the quantitative determination of the elements is based on the intensity of the gamma rays. The analytical method was validated with a Marine Sediment Reference Material MESS-1 (NRCC). The results are presented in Table 2.

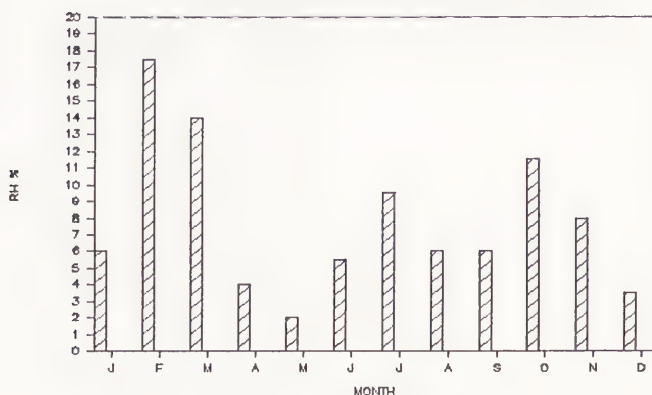
X-ray Diffraction

The salt samples were analyzed by x-ray powder diffraction using a Guinier-deWolff focusing camera with copper radiation ($K\alpha=1.5418\text{\AA}$). The sample which was finely ground into minute crystals, was applied to an adhesive substrate, and irradiated in transmission mode with monochromatic radiation. Since the crystals are randomly oriented a proportion of them will satisfy the Bragg condition $n\lambda=2d\sin\theta$ where θ is the angle at which constructive interference occurs, n = an integral number, λ = wavelength of the radiation used, and d = the interplanar spacing for the planes giving rise to the coherent scattering. In this procedure the crystal lattice planes with a specific spacing (d) result in refractions which strike the photographic film in a series of arcs forming the diffraction pattern on the film. The crystal lattice (d) spacings are determined by measuring the distance between the arcs which are then compared to the lattice spacings of known minerals. The intensity of the x-rays is determined by the degree of darkening of the arcs. The diffraction patterns were compared to standard patterns in the Joint Committee on Powder Diffraction Standards (JCPDS) File (Table 4) and the d -spacings and intensities are presented in Table 3.

GRAPH 1
MAXIMUM/MINIMUM MONTHLY RH



GRAPH 2
MAXIMUM DAILY FLUCTUATION RH



Results

The results of Neutron Activation Analysis indicate the elemental composition of the salts from which may be estimated the molecular weight of the compound(s) and the ratio of elements in the molecular formula. The molecular weights (based on one atom of calcium per molecule) may be determined by dividing the molecular weight of calcium by the weight % calcium and multiplying by one hundred. The results fell into two groups with samples 2, 6, 7, 8, 9, and 11 having molecular weights between 160 and 260 whereas the remainder had molecular weights between 550 and 1000 based on one calcium atom per molecule. The ratio of calcium to chlorine suggests a 1:1 ratio for samples 2, 6, 7 and 11 but a ratio of approximately 1:3 for samples 1, 3, 4, 5, 10 and 12. For samples 8 and 9 they appear to have approximately 3 chlorine atoms for each calcium atom.

The eight XRD patterns were compared to those of the common soluble salt compounds, including several compounds based on calcium acetate, as well as to those of "efflorescence x" published by FitzHugh and Gettens (2).

Table 2 NAA Results

sample no	ELEMENTS (conc.in ppm or wt.% where indicated)							
	Mg	Na	Cl	Al	Mn	Ca	Ti	V
1	0.16% ±0.03	0.061% ±0.015	15% ±5	0.047% ±0.003	8 +1	5% +1	n.d.	n.d.
2	0.31% ±0.04	0.100% ±0.02	13% ±1	0.27% ±0.02	39 ±2	18% ±2	366 ±70	5.7 0.7
3	0.28% ±0.04	0.120% ±0.02	13% ±1	0.43% ±0.02	51 ±2	5% +1	323 +80	7.6 ±0.9
4	2.1% ±0.4	0.78% ±0.07	15% ±1	0.68% ±0.04	123 ±8	4% +1	<200	30 ±3
5	0.30% ±0.05	1% ±0.06	16% ±1	0.53% ±0.03	100 +3	5% +1	n.d.	13 ±2
6	0.77% ±0.07	0.34% ±0.04	14% ±1	0.19% ±0.01	72 +8	15% +2	n.d.	9 +1
7	n.d.	0.06% ±0.02	21.5% ±0.1	0.29% ±0.004	42 ±20	22.2% ±0.4	<200	3.5 ±1.4
8	0.75% ±0.16	0.39% ±0.02	4.6% ±0.05	1.6% ±0.008	335 ±14	15.24% ±0.36	0.23% ±0.02	29 ±1.6
9	0.57% ±0.07	0.26% ±0.03	8.8% ±0.8	0.76% ±0.04	194 ±6	24% +3	n.d.	15 +2
10	0.30% ±0.05	0.100% ±0.02	12% +1	0.57% ±0.03	105 +5	7% +2	460 +100	11 +1
11	0.37% ±0.16	0.14% ±0.02	12.2% ±0.09	0.88% ±0.006	152 +16	19.1% ±0.4	811 +200	19 ±1.6
12	0.48% ±0.06	0.25% ±0.05	13% ±1	0.87% ±0.04	100 +3	5% +1	818 ±150	11 ±2

n.d.= not determined

Table 3 XRD Results

sample no. 12		sample no. 11		sample no. 7		sample no. 8	
d	I	d	I	d	I	d	I
8.40	90	13.5	30	8.35	90	7.40	10
6.95	30	10.8	20	6.95	20	7.00	90
6.05	20	8.40	10	6.05	15	6.40	80
4.85	5	7.00	5	4.82	15	4.30	3
4.20	10	6.20	30	4.21	20	4.00	4
3.45	5	4.30	5	3.68	10	3.92	3
3.38	80	3.45	90	3.36	80	3.53	3
3.28	100	3.34	100	3.28	100	3.50	2
3.10	30	3.26	5	3.08	10	3.40	70
3.04	50	3.09	10	3.01	30	3.35	80
2.96	10	3.04	10	2.44	30	3.31	60
2.92	3	3.00	5	2.42	20	3.07	20
2.72	2	2.96	5			3.05	3
2.68	5	2.47	5			2.98	5
2.44	4	2.45	3			2.41	5
2.42	30	2.39	2				
2.40	20	2.26	6				
2.09	3	2.25	3				

sample no. 1		sample no. 3		sample no. 2		sample no. 10	
d	I	d	I	d	I	d	I
7.40	100	13.30	10	13.70	5	13.70	10
6.05	30	10.60	20	10.80	10	10.70	30
5.95	20	8.04	10	7.40	40	8.40	5
4.41	10	7.00	5	7.00	20	6.30	30
4.20	30	6.30	5	6.30	20	6.20	30
3.72	5	6.20	5	6.20	30	3.43	100
3.67	10	6.10	30	4.42	5	3.39	5
3.42	10	4.20	5	4.12	20	3.32	20
3.35	40	3.44	100	3.72	5	3.08	20
3.25	90	3.35	60	3.68	5	3.04	5
3.21	5	3.27	10	3.45	100	2.45	3
3.19	3	3.08	10	3.36	40	2.43	3
3.09	10	3.03	10	3.35	40	2.28	3
3.03	50	2.97	5	3.27	30	2.25	5
2.98	5	2.94	5	3.08	20	2.23	3
2.95	10	2.66	3	3.02	20		
2.89	5	2.46	5	2.43	15		
2.66	10	2.44	7	2.21	8		
2.44	40			2.16	5		
2.42	20						

Table 4 XRD Patterns of Known Compounds

calclacite Ca(CH ₃ COO)Cl·5H ₂ O (JCPDS no. 12-869)		calcium acetate acetic acid (CH ₃ COO) ₂ Ca·CH ₃ COOH (JCPDS no. 10-781)		calcium acetate hemi hydrate (CH ₃ COO) ₂ Ca·0.5H ₂ O (JCPDS no. 14-792)	
d	I	d	I	d	I
8.27	s	9.76	80	16.7	100
6.87	m	6.70	10	11.8	80
6.15	w	6.45	100	8.59	80
4.86	vw	6.18	60	8.34	40
4.16	m	6.10	10	7.44	60
3.67	w	5.04	10	6.94	40
3.24	s	4.96	20	6.34	40
3.06	w				
3.00	w	4.72	10	5.54	40
2.94	vw	4.42	10	5.24	10
2.65	w	4.18	20	5.13	20
2.43	s	3.74	60	5.02	10
2.30	m	3.65	10	4.48	10
2.22	w	3.60	20	4.37	20
2.14	w	3.43	80	4.16	20
2.04	m	3.41	60	3.93	10
1.907	vw	3.35	100	3.84	40
1.876	vw	3.23	80	3.66	10
1.842	w	3.10	10	3.51	60
1.704	w	3.07	20	3.41	40
1.560	vw	2.90	40	3.34	20
1.486	w	2.83	10	3.28	60
		2.71	20	3.21	40
		2.65	10	3.01	10
		2.59	20	2.95	10
		2.53	10	2.91	10
		2.47	10	2.86	10
		2.44	40	2.68	20
		2.42	20	2.64	10
		2.40	10	2.61	10
		2.36	10	2.55	10
		2.29	10	2.51	10
		2.27	60	2.38	20
		2.24	20	2.34	10
		2.22	10	2.27	10
		2.16	10	2.18	10
		2.13	10	2.14	20
		2.10	20	2.10	10
		2.09	20	2.06	10
		2.06	40	2.04	10
		2.05	10	2.01	10
		2.01	10	1.98	10
		1.99	10	1.96	10
		1.95	20	1.94	10
		1.91	10	1.88	10
		1.89	20	1.85	20
		1.88	10	1.76	20
		1.86	10	1.71	10
		1.80	10		
		1.78	10		
		1.77	40		
		1.72	20		
		1.69	10		
		1.65	20		
		1.64	10		
		1.61	10		
		1.57	20		
		1.53	10		
		1.50	20		
		1.49	10		
		1.41	10		

s = strong, m = medium
w = weak, vw = very weak

A comparison of diffraction patterns reveals a pattern for sample 7 which is essentially pure calclacite, calcium acetate chloride pentahydrate (Ca(CH₃COO)Cl·5H₂O) (3). Calclacite can be identified as the major component in sample 2. The patterns of samples 1 and 12 show major quantities of calclacite and traces of the same pattern are evident in sample 3. The compound (or compounds) giving rise to the patterns of samples 10 and 8 has (have) not been identified.

A comparison of calcium to chlorine ratios with the XRD results reveals a one to one ratio for samples 2 and 7 which coincides with calclacite as the major phase. The molecular weights of samples 2 and 7 are in the range for calclacite (225) as is sample 11 for calcium acetate acetic acid (218).

Conclusion

It is postulated that calclacite formed by the reaction of calcium in the ceramic fabric with acetic acid emitted from the wooden storage materials in combination with residual chloride from previous treatment of the ceramics with hydrochloric acid (1) (2). The unidentified components in several of the samples could be decomposition products of calclacite, different hydrates of this compound, or more complex crystalline salts containing several metal atoms. The samples with excess calcium (1, 3, 4, 5, 10 and 12) may well be of the type Ca(CH₃COO)Cl·Ca_xX_m in a double salt where X may be CO₃ or CH₃COO⁻ or SO₄²⁻ etc. For samples 8 and 9, since they have more chlorine present, X might be chlorine or they could be mixtures such as calclacite and CaCl₂·2H₂O, for example.

Further study of the efflorescence found in the Agora ceramic collection will encompass the analysis of fabric from 72 ceramic objects as well as samples of efflorescence from 50 of these ceramic objects. The ceramic fabric will be analyzed by SEM and the salt samples will be analyzed by both SEM and XRD. Represented among these samples to be analyzed are the three salt morphologies as well as a variety of ceramic fabric types, porosities and firing temperatures. The objects sampled range in history from the 6th c. B.C. to the 5th c. A.D. and are characterized by different provenances. Included in the 72 fabric samples are 22 "standards" which were taken from objects similar in fabric, date, and provenance to those objects which were sampled for efflorescence but which were themselves free of salts. 65 of these samples were taken from objects housed in the same storeroom and storage cabinets as the twelve objects discussed in the present article.

References

- 1) Taboury, M.F. "Des Modifications Chimiques de Certaines Substances Calcaires Conservees dan des Meubles en Bois", Bulletin de la Societe Chimique de France, 49 (1931), 1289-1293.
- 2) FitzHugh, E.W., Gettens, R.J., "Calclacite and Other Efflorescent Salts on Objects Stored in Wooden Museum Cases", Science and Archaeology, Cambridge, MA, 1971, 91-102.
- 3) Van Tassel, R. "On the Crystallography of Calclacite, $\text{Ca}(\text{CH}_3\text{COO})\text{Cl} \cdot 1.5\text{H}_2\text{O}$ ", Acta Crystallographica 11, part 10 (Oct. 1958), 745-746.

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I wish to thank Professor R.D. Heyding and Professor J. Poland in the Department of Chemistry, Queen's University, Kingston, Ontario, Canada for their assistance with the analysis of the salts and the interpretation of the results.

Working Group 21

Training in Conservation and Restoration

Formation en conservation et restauration



ABSTRACT

THE NEED FOR TRAINING PERSONNEL FOR THE CONSERVATION OF CULTURAL HERITAGE IN ASEAN COUNTRIES

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Introduction

ASEAN countries namely Brunei Darussalam, Indonesia, Malaysia, Philippines, Singapore and Thailand are in a region which is rich in Cultural Heritage both movable and immovable. This Cultural Heritage is very unique and significant to each country, each of which has a long history. These countries are located in the tropical zone characterized by a hot and humid climate. Such climate causes the deterioration of all kinds of cultural materials with resultant external and internal changes of the materials. Therefore the conservation problems in ASEAN countries are more acute than in temperate climate countries. Even so, it seems that the government of each country places the conservation of cultural heritage at a low priority regarding the allocation of funds. Therefore the lack of trained personnel and well equipped conservation laboratories are basic problems facing ASEAN countries attempting to preserve their cultural heritage.

Types of Cultural Material

ASEAN countries are rich in both movable and immovable cultural heritage. Movable cultural heritage is mostly archaeological objects, ethnographical objects, natural history and fine arts. These have different chemical and physical properties based on the type of materials from which they are made. These include metal, textile, stone, wood, leather, ceramic, paper, manuscript, natural science collections and paintings. Some are very sensitive to the change of climate while the others are more durable. The most sensitive cultural material is that made of organic material such as paper, wood, textile, manuscript, leather, bone and ivory etc. By nature the materials are a good nutrient for insects and micro-organisms. The damage or deterioration of the cultural materials can cause both physical and chemical changes which are irreparable or repairable.

Immovable cultural heritage includes ancient, historical monuments and sites are made of different building materials such as brick, stone, laterite, wood and combinations of these. They can be degraded, disintegrated and damaged due to many local factors. The climatic condition is the most important factor causing damage, and inducing the deterioration of building materials resulting in the growth of micro-organisms, erosion of materials, chemical and physical changes, especially where moisture is encountered.

Climate

ASEAN countries are located in a tropical zone characterized by a hot and humid climate with high light levels and heavy rainfall throughout the year. This climate causes the deterioration of all kinds of material. High relative humidity causes the growth of micro-organisms on cultural materials, not only on those made of organic material but also on the building materials of monuments, i.e. stone and brick, resulting in the staining, degradation or disintegration of the materials. In addition the warm climate provides ideal conditions for insect attack, therefore the problems caused by insects, especially termites, are very serious in this region. Because of high light levels the degradation and disintegration of paper, textile, photographs and paintings are also a serious problem.

Present Situation Concerning the Conservation of Cultural Heritage in ASEAN Countries

At present the conservation of cultural heritage in ASEAN countries is in general only at a basic level. There are many problems encountered with the conservation of cultural heritage in this region. One problem is the lack of qualified personnel. There are very few professional conservators to carry out the huge task of conserving ASEAN's cultural heritage.

Conservation involves an understanding of the methods and materials of construction of the objects and their uses. The causes and mechanisms of deterioration have to be studied followed by the chemical and physical procedures necessary to conserve the objects. Therefore the conservation of cultural material requires a scientific background to study the cultural materials and the conservation procedures. That is a chemist or scientist, or one who has a chemistry background will be required to carry out these kinds of work.

ASEAN countries namely Brunei Darussalam, Indonesia, Malaysia, Philippines, Singapore and Thailand are in a region rich in Cultural Heritage. This Cultural Heritage is very unique and significant to each country, all of which have a long history. Due to the location which is in a tropical zone characterized by heat, humidity and heavy rainfalls, the deterioration to various kinds of cultural materials are very acute. However, the professional conservators for the conservation of cultural heritage of the countries are very few. Each country needs trained personnel to carry out the conservation of the cultural heritage. The facilities for training personnel in the conservation of cultural heritage in this region are limited, so that assistance from other institutions where they have progressed in the field of conservation will be most welcome.

The author has had the chance to visit many ASEAN countries and received information from the Heads of conservation laboratories and others who work on the conservation of cultural heritage in each country, on the conservation situation, staff, facilities, area of experience and type of collections. She has found that every country faces various conservation problems and needs more trained personnel at professional level, more facilities, exchange of experiences and relevant publications, in order to carry out the proper conservation of their cultural heritage. In the past decade, every country in ASEAN has realized the importance of the uniqueness and significance of their cultural heritage, therefore there are many projects concerned with culture being carried out between ASEAN countries. One of the projects under the SEAMEO Project on Archaeology and Fine Arts (SPAFA) provides short training courses (see Appendix I) for member countries on the conservation of various objects and is carried out by the Conservation Sub-Division, Division of National Museums, Fine Arts Department in Bangkok. Even so, this is still not enough compared to the conservation work which needs to be carried out. If the cultural heritage of ASEAN countries is to be preserved, more trained personnel at professional level will be required.

The recent survey by the SPAFA Regional Centre of the conservation laboratories and facilities in the SEAMEO countries indicated the following :

<u>Country</u>	<u>Name of Institute</u>	<u>Main types of collections</u>	<u>Number of staff and qualifications</u>
1. Brunei Darussalam	Conservation laboratory, National Museum	Museum objects	1 chemist 3 technicians
2. Indonesia	- Conservation laboratory, National Museum, Jakarta - Conservation laboratory, Borobudur, Jakarta	Museum objects Monuments (stone)	no information "
3. Malaysia	Conservation laboratory, National Museum, Kuala Lumpur	Museum objects	1 technician (just started)
4. Philippines	National Museum, Manila	Museum objects	1 chemist 6 chemical engineers 6 technicians
5. Singapore	National Museum	Museum objects	2 technicians
6. Thailand	Conservation Sub-Division, Division of National Museum, Fine Arts Department	Museum objects	6 chemists (Ph.D,B.Sc)/ conservators 10 technicians

The information indicates that additional qualified personnel are required when compared with the great wealth of cultural heritage in each country. To solve this problem a UNDP/UNESCO Project on the Conservation of Cultural Property was prepared by Dr. Colin Pearson (a UNESCO consultant), and has been approved. This project aims to raise the professional conservation level in ASEAN countries by sending 1 person for 2 years or 2 persons for one year each, to be trained abroad in a specific area of conservation. The second aim is to promote the establishment of a network of conservation laboratories throughout the ASEAN countries. This project is now going on, but it is rather difficult to achieve the goals since many countries under the UNDP/UNESCO Project can not find suitable qualified persons to be sent for training.

Facilities for Conservation Training in ASEAN Countries

Each country has a different level of conservation staff, facilities and equipment. Few conservators have gained formal tertiary conservation qualifications. The majority have only been trained through short courses such as run by SPAFA in Bangkok, Thailand, the National Research Laboratory for the Conservation of Cultural Property (NRLC), Lucknow, India or ICCROM in Italy. These courses can only provide a basic understanding of the conservation of cultural property, because the background knowledge of trainees is often lower than a first degree and does not include chemistry. Therefore the program of training courses carried out by the Fine Arts Department in Bangkok for SPAFA has to be adjusted in order to be suitable for the trainees. The year-long academic training course will provide more theory and practice and will be useful in order to raise the professional level in this region,

but the problem is still that most of the ASEAN countries can not get qualified personnel to be sent for such training.

Conclusion

As described above needs of the professional conservator in ASEAN countries needs urgent attention, and the level of conservation of cultural heritage in ASEAN countries must be raised. Assistance from other institutes which are advanced in the field of conservation of cultural heritage would be very welcome.

Appendix I

SPAFA Training courses carried out by the Conservation Sub-Division, Division of National Museum, Fine Arts Department, Bangkok, Thailand

- 1. Conservation of Underwater Archaeological Objects

<u>Duration</u>	3 months
<u>Date</u>	1. December 1978 - March 1979
	2. December 1979 - March 1980
	3. March - May 1984

- 2. Conservation of Bronze Objects

<u>Duration</u>	3 months
<u>Date</u>	1. April 16 - July 15, 1979
	2. July - September 1980
	3. September - December 1983

- 3. Research Methods of the Conservation of Organic Material

<u>Duration</u>	3 months
<u>Date</u>	1. October 1982 - January 1983
	2. February 12 - April 12, 1985

- 4. Preventive Conservation of Museum Objects

<u>Duration</u>	2 months
<u>Date</u>	1. November - December 1987
	2. October 8 - December 8, 1989

ABSTRACT

The ICOM Committee for Conservation Working Group on Training in Conservation and Restoration started in 1983 a long term project concerning the collection of theses, diplomaworks and research reports produced by conservation training institutions on an international level. Based on a first edition, published in 1987 by the National Centre of Museums in Budapest, Hungary, an updated and enlarged edition covering more than 3000 titles from 49 institutions in 21 countries has been compiled using a database including a subject and author index. The mode of the selection and structure used for the compilation of the bibliography and the reference system is described. The publication of the bibliography could be realized by the financial support and collaboration of ICCROM.

KEYWORDS

BIBLIOGRAPHY, TRAINING INSTITUTIONS, DIPLOMAWORKS, ACCESS, THESES, RESEARCH.

BIBLIOGRAPHY: THESES, DISSERTATIONS, RESEARCH REPORTS IN CONSERVATION

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Introduction

The project to collect theses, diplomaworks and research reports in Conservation was at first proposed by Christoph von Imhoff, the former Coordinator of the ICOM Committee for Conservation, Working Group on Training in Conservation and Restoration on the occasion of the group's interim meeting in Dresden 1983 and the first results were discussed at the ICOM-CC 7th Triennial Meeting in Copenhagen, 1984 (1). Seven years later, again in Dresden, it is now possible to present a second and enlarged edition of the bibliography so far compiled.

The main intention of the project was to demonstrate the range of topics and results having already been achieved by students undergoing training in the different fields of conservation. Furthermore and even more important it was the goal to facilitate access to this important material which is often buried in institutional libraries.

1st Edition of the Bibliography

A first edition of the bibliography was presented on the occasion of the Sixth International Restorer Seminar in Veszprem (Hungary) 1987 (2). The publication was realized by the support of the National Centre of Museums in Budapest which took responsibility for the printing and the distribution of 500 copies of the bibliography (3).

The first edition covered seminar reports, diploma works, theses and research reports from 31 training institutions in 15 countries. Approximately 1500 titles were incorporated in the bibliography. The listing started in general from 1975 onwards. It should be noted that the editors did not judge the standards of the diplomaworks and theses collected which probably vary according to the type and to the level of the respecting training programmes in which they were carried out. This means that as a result the complete listing relied exclusively on the information provided by the specific training institutions supporting the collection of the material. In addition a number of titles of so-called "grey literature", mainly internal text books or teaching aids, catalogues, booklets, reports, bibliographies etc., have been incorporated in the first edition.

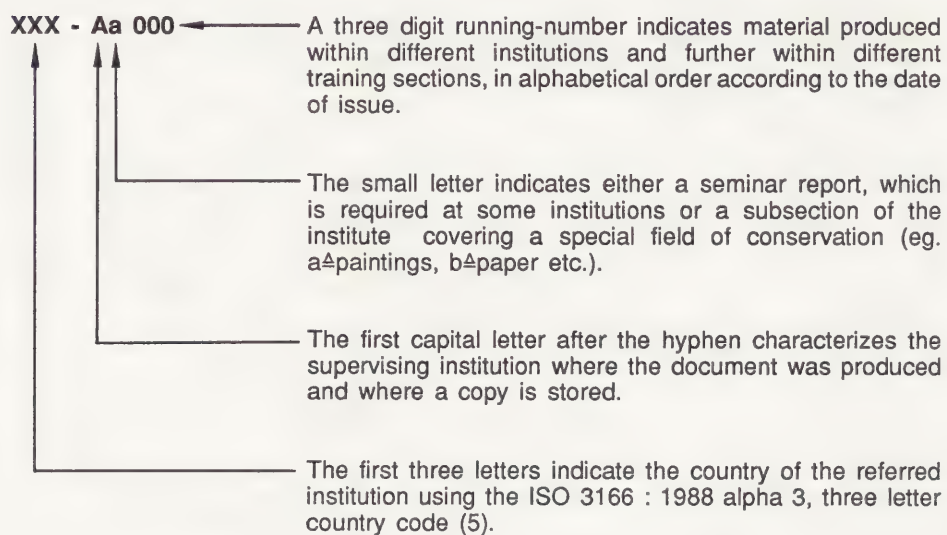
The lists of the United Kingdom training institutions were compiled by Peter Winsor, The Conservation Unit in London, who published a separate survey already in 1985 and gave permission to incorporate this material in the bibliography (4). The listing of the North American training institutions was realized by Rebecca Anne Rushfield, New York.

2nd Edition of the Bibliography

The demand for the bibliography led to the decision to carry on with the project. During the last 3 years the material collection was updated and extended by incorporation of additional training institutions and covered up to March 1990 approximately 3000 titles from 41 training institutions in 18 countries. The listing followed in general the system developed for the first edition and was carried out again in close cooperation with Peter Winsor and Rebecca Anne Rushfield.

The increase in collected material made it necessary to use a database for processing the information. The used database is IBM compatible and facilitates indexing and future extension of the bibliography.

In regard to the original plan to produce a bibliography as complete as possible at an international level, the reference system used by Peter Winsor was adopted and extended for the corresponding bibliography of European and North American institutions, as illustrated in the following example:



The bibliographical data was specified and listed in the following manner:

- Alphabetical order of the ISO country code.
- Code of institution
- Code of subsection of institution (special field of conservation, eg.: paintings conservation)
- Date of issue
- Name of author in alphabetical order

The codification used for the specific institution was chosen according to the date of receipt of the information provided. This was necessary in order to make the updating operation in the future easily possible without changing the codes.

The adopted computer programme made it additionally possible to generate an author index as well as a subject index. For the subject index the data was indexed according to the given title using two descriptive fields. The first characterizes the main material group of which the mentioned subject consists, while the second field supplies information concerning the specific conservation treatment performed.

To give an example: the title "The history, techniques and conservation of paintings on copper supports. A preliminary survey." (Horovitz) was indexed on 'paintings' for the material group, and 'on copper, history, technology, conservation' for the describing field.

Titles which do not contain sufficient information could not be considered in the index.

Due to the lack of a bibliographical database, 'Dbase III plus' (R) was adopted to fit the above mentioned requirements. The sorted data was then edited using the "Ventura" (R) desk top publishing software and finally published by ICCROM.

The present status of the bibliography remains still incomplete as a number of institutions could not be incorporated until now. Besides the fact that no funds were guaranteed until now to cover the expenses for the project so far, the main problem seems to be the lack of volunteer collaborators in institutions to support the project with the required lists of titles in the original language, and in addition the translation of titles in English. Although there is in general a positive intention to support the project, the reason for this lack of collaboration is that most institutions have not enough time and personnel to provide the required information.

In the opinion of the authors an important part of the 1983 proposed project has been realized by compiling the bibliography on a database, and furthermore since ICCROM have offered to support the project by funding the publication of the 2nd edition of the bibliography. From the beginning ICCROM was regarded as the ideal institution to distribute the information and encourage international cooperation in this field.

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References

1. Gabriela Krist, Gerhard Banik: "Survey of Source and Access to Students Reports and Theses", ICOM Committee for Conservation, Working Group Training in Conservation and Restoration, 7th Triennial Meeting, (Copenhagen 1984).
2. Gabriela Krist: "Zum Stand der Sammlung von Diplomarbeiten und Forschungsberichten auf dem Gebiet der Restaurierung", Sixth International Restorer Seminar, Veszprem 1987, (Preprints, Budapest 1988): 395.
3. Gabriela Krist, Gerhard Banik, Sebastian Dobruskin, Rebecca Anne Rushfield, Peter Winsor: "Bibliography, Theses, Dissertations, Research Reports in Conservation", (Budapest 1987).
4. Peter Winsor: "Theses and Dissertations in Conservation from United Kingdom Training Institutions", British Museum, Department of Conservation, (London 1985).
5. ISO 3166 : 1988: Code for the Representation of Names of Countries (Switzerland International Organization for Standardization, 1988).

ABSTRACT

The main idea behind this specialized branch are the complex conceptions and aspects of architectural and art history as well as of monument preservation includes the characteristics of both the interior and exterior the function of the building, its colour and mural painting. The training can be divided into theoretical basis of the methods and technology of conservation and restoration of mural painting and coloured architectural design, scientific investigations, lectures of history of art and architecture.

The training of restorers for historic murals and coloured architectural design at the Dresden Academy of Fine Arts

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Introduction

Since 1985, the Dept. of Restoration at the Dresden Academy of Fine Arts has been holding a 5 year degree course in the conservation and restoration of historic murals and coloured architectural design. The main idea behind this specialized branch is that all important historic buildings were designed for a specific purpose and create a certain unity of architectural and artistic design including their interior design. The complex conception of a building and its furnishings as an integral work of art demands a broader curriculum than the traditional courses offer. The attempt is being made to include all aspects of architectural and art history as well as of monument preservation in order to clarify the original inherent intention and characteristics of both the interior and exterior of the building as well as its colour and painting. Only in this way can we understand the changes in function and form which have taken place over the years as a historical unity to be explained through research and documentation. This basis enables an objective evaluation of specific details or larger interrelations leading to a set conception of the conservation and restoration of murals, paint layers, architectural sculpture and the movable decoration on facades and interiors, right up to possible reconstruction.

Course Contents

For such a comprehensive conception of architecture, detailed knowledge of the specialist theory involved is needed. This can be divided into materials technology, methods of conservation and restoration, disciplines of natural sciences, architecture and art, specialist experience and a good artistic training. A restorer should be trained to develop an awareness of the problems in the practical preservation of monuments. With his/her specialized knowledge and ability, he/she ensures the up-keep of valuable buildings and historical works of art; with high-quality, specialized work, he/she determines the end result in terms of conservation and aesthetic restoration, and must, therefore, be aware of his/her moral and material responsibility for the work. To achieve this goal, the course is divided into several subjects.

Conservation and restoration of mural and architectural paintings

Theoretical basis: general historical synopsis of the development of murals and associated technology. Damage to buildings, types of damage to paintings and their supports. Technology of restoration, conservation and materials. Practical work: conservation of supports (plaster, wood) and of the paint layer. Removal, cleaning, retouching and transfer of murals. Restoration, after-care and documentation.

Research, conservation and restoration of historical architectural paints for exterior and interior use

Theoretical basis: Historical synopsis of the development of coloured architecture from ancient times to the present. Special features of style and material technology. Scientific analyses of pigments and binding agents.

Practical work: According to architectural history and building condition and using a wide variety of investigation methods, find of coloured architecture are determined, their connection and stratigraphy documented and the colour systems interpreted. With the help of laboratory analyses, the final result of the documentation is used to produce a preservation goal for the conservation, restoration or reconstruction of an architectural colour. The practical training for conservation and restoration

takes place in connection with the subject of mural painting.

The specialized training in both these fields is carried out predominantly on site, on a building within the GDR, thus encouraging direct contact between the different specialists (art historians, scientists, architects and craftsmen). Work on site is intensive and demands dedication; it depends mainly on division of labour, is extensive and time-consuming. So the student must develop certain physical abilities for his/her future career. Other vital knowledge gained during this period of practical training includes efficient planning, organization and coordination of labour as well as the basics of cost calculation. The practical training on site is carried out in collaboration with the Institute for the Preservation of Historic Monuments, preservation companies and other such organizations to draw up a cultural contract to serve the agreed goal.

Conservation and restoration of architectural details (architectural sculpting, interior decoration) made of wood, stone and canvas

Theory and practice of the restoration of wood and stone; the relining of canvas pictures and the cleaning of pictures are taught by a specialist with reference to the particular building. The aim of the subject "Architectural details" is to demonstrate the conservation and restoration of secondary genres. By virtue of his more complex work involving the whole structure, the restorer for mural painting and coloured architectural design has the task of fixing the goal of preservation and restoration also for interior design. Thus, he/she must be familiar with the special problems associated with this in order to be able to incorporate this special branch of restoration into the overall task.

Technical and artistic foundations, practice of painting techniques, and copying

The theoretical basics and practical work cover: techniques for gilding murals; special material simulation techniques; basics of murals (humans, still life); design of murals and their completion in fresco and secco on the wall; reproduction of historical models in fresco and secco; free transfer of murals according to patterns in secco.

The training in conservation and restoration is considerably assisted and supplemented by artistic training. The objective of this subject is to familiarise the students with the special working methods as an expression of the individual artistic epochs. At the beginning, free studies are prepared that train and sensitise the students in the single steps such as sketching, drawing and the execution of mural painting in various techniques. Furthermore, the preparation of copies is an integral part of this field of training in order to get an insight into historical painting techniques. The knowledge gained will help the student analyse historical materials and the painting technique to be able to easier identify any damaging effects.

Scientific investigations

Theory and practice: Analyses into pigments and binding agents of objects treated in mural painting and coloured architectural design; scientific photography and endoscopy.

The subject of scientific investigations is also very closely associated with the principal subjects. The goal of training is the independent preparation of the samples in the lab and the interpretation of the analysis results.

History of art and architecture

This subject embraces essentially special lectures held by outside experts on specific aspects of mural painting, coloured architectural design, research into building construction and iconography.

In the field of history of art and architecture, lectures on the latest research results in mural painting and coloured architecture are delivered by prominent investigators. This is to make the students conversant with the interrelations to which can be assigned a building with its artistic details.

Seminar projects

Subjects: technological, stylistic or scientific investigation and documentation of the history, development or materials technology of murals and coloured architecture.

The seminar paper is the result of the student's own research and is a contribution to the progress of technology or art history.

Summer practical work

The four-to-five week period of practical training in the summer serves to deepen and supplement the course.

Excursions

Excursions lasting one day or more at home or abroad underline certain important aspects of murals and coloured architecture.

Diploma paper

The fifth year of the course is devoted exclusively to the diploma paper. The subjects and objects for the paper are selected so that the student takes a large part of the responsibility for a general restoration project. To ensure that the student can personally complete or supervise the completion of the project if this extends beyond the course (partial projects are standard), one building within the student's field of future activity is preferred.

ABSTRACT

To meet the rapidly escalating problem of conserving industrial collections, the Science Museum (London) offers a new three-year training course. The syllabus is mainly a practical one for skilled craftsmen, but a series of study sessions supplies the essential theoretical background. Independent examiners regularly assess each student's work and successful completion of the course leads to the awarding of the Certificate in the Conservation of Industrial Collections.

KEYWORDS

Conservation, industrial collections, training, United Kingdom.

CONSERVATION OF INDUSTRIAL COLLECTIONS - A NEW TRAINING COURSE

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Introduction

In recent years, industrial collections have grown at a phenomenal rate in the United Kingdom: many new museums specialize in aspects of industrial history; museums have been established on industrial sites, and numerous non-specialist museums now acquire industrial materials. Even within long-established museums of industrial history, the size and scope of the collections is greater than ever, as unfamiliar modern materials take their place alongside the traditional metals and wood. The conservation of these collections is not as developed as it is in, for example, fine arts and archaeology; rather, their care has often been more akin to industrial maintenance, usually based upon traditional craft skills executed to a very high order but all too frequently lacking the rigour and discipline of modern conservation practice.

To address this problem, the Conservation of Industrial Collections Forum (CICF) was established in 1987. Under the Chairmanship of the Director of the National Museum of Science and Industry (the Science Museum), this group of conservators, curators, engineers and restorers has considered how the conservation of industrial material might be raised to the same standard as that for other collections.

The Forum identified staff training as the most urgent priority. The problem was seen as twofold: first, concern at the loss of traditional engineering craft skills; second, the need for a conservation approach based on a methodical study of the objects, their history, deterioration and treatment, of which a written record is made. The code of practice for the conservation of industrial artefacts should be the same as that for other museum collections. As none of the existing training courses was thought to be appropriate to meet the special challenge of industrial collections, the CICF approved a wholly new syllabus drawn up by their Training Sub-Committee. The Science Museum acts as the parent body for this Conservation of Industrial Collections Training Course.

It was recognized that craft skills and experience are essential to most of the work on industrial artefacts and that conservation training should be an extension of this, building on the present strength in the field - the skill, knowledge and enthusiasm of the staff. The course is, therefore, available only to people already employed in conservation or restoration work, most of whom are technicians working in museums or a few commercial firms. To make the system of assessment manageable, and to encourage open discussion after lectures, each class is restricted in numbers: about ten to twelve students is considered the optimum. For these reasons also, the course is at present available only to people working in the United Kingdom.

Syllabus

The duration of the course is three years. It comprises three main elements:

- a. Practical work on objects.
- b. Special project.
- c. Theoretical studies.

- a. Practical Work

The course is a practical one for practical people and much of the students' time is devoted to learning how to apply their technical expertise in a manner which meets present-day conservation standards. This practical work is carried out at the place of their employment and the students are required to spend at least eighty per cent of their time working on the conservation of objects. To make the scheme operable, the course work must be fitted in with the priorities of the students' employers. At the beginning of the academic year a member of the Science Museum team agrees with each workforce supervisor a programme of work for several months ahead - how long this might be depends on the local circumstances. The agreement is updated as the course progresses and a new programme is agreed when that in hand nears completion.

Naturally, students working in different workshops will have a different degree of diversity in their routine work. However, it is essential that they should all experience a wide range of techniques if they are to become competent conservators. To this end, a syllabus of practical work has been drawn up, of which all students must gain at least some experience or knowledge. This comes under thirteen general headings:

- | | |
|------------------------------|---|
| i. Safety at work | viii. Joining metals |
| ii. Conservation records | ix. Moulding and casting |
| iii. Cleaning techniques | x. Woodwork techniques |
| iv. Consolidation techniques | xi. Identification of materials |
| v. Adhesives and fillers | xii. Environmental monitoring and control |
| vi. Protective coatings | xiii. Problems with working exhibits. |
| vii. Metalwork techniques | |

Each of these areas is sub-divided into more specific skills. A fully detailed list is outside the scope of this paper, but the following example may be regarded as typical:

Cleaning Techniques

1. Solvents, including paint removers.
2. Chemical cleaning: acids, alkalis, soaps, chelating agents.
3. Steam.
4. High-pressure water.
5. Bead-blasting and air-abrasion.
6. Abrasive cleaning by hand using: wire wools, metal brushes, glass-bristle brushes, plastic pads, carborundum and other abrasive sheets or pads; polishing pastes and powders.
7. Abrasive cleaning by machines, grinding, buffing wheels, polishers.
8. Vibro tools and needle guns.
9. Ultrasonic tanks and picks (Cavitron).
10. Flame cleaning.
11. Electrolytic cleaning.
12. Safety for operator and object in all the foregoing.

Some of the more specialized techniques are taught as practical work during the theoretical study sessions.

It is unrealistic to expect every student to become an expert in all the skills, so a compromise divides the levels of attainment into three acceptable grades:

i. Skilled

The student is able to undertake the technique safely, confidently and to a high standard on a variety of objects. He also demonstrates an ability to adapt and develop the technique to meet different circumstances and is able to teach the process to others. It is expected that those students already skilled in any technique will act as tutors to others on the course.

ii. Familiar

The student knows enough of the theory and practice of the technique to carry out work when it is relatively straightforward, and is sufficiently familiar with it to judge the quality of someone else's work. He is competent to write detailed specifications for contract work but knows his limitations.

iii. Aware

All students should have at least an awareness of the skills and materials which each technique demands. This requires that they have seen it demonstrated, have made at least one attempt at it themselves under skilled tuition, and know something both of its potential and its disadvantages.

The placing of Safety at Work as the first of the areas of experience is deliberate. All students must be thoroughly familiar not only with what the law requires of them, but how they should approach their work for their own safety as well as that of their colleagues and the objects on which they are working. How much emphasis needs to be laid on any of the other areas depends on the student's background. It is envisaged that, of the three levels of competence, each student should attain the highest skilled level in about one third of the techniques, be familiar with another third and be aware of the remainder.

The student is responsible for preparing reports on all the work carried out and compiles a portfolio which is presented at the end of the three years for assessment by the examiners.

b. Special Project

In the third year each student undertakes a special six-month project in which an object (or a group of objects) is treated to an in-depth study. This includes not only a more rigorous consideration of the conservation requirements but also the historical and technological significance of that object. In this way, the student should become more appreciative of the

curatorial aspects of museum work and sympathetic to the attitudes of others who are equally concerned with the welfare of the collections. A detailed report on this project forms an important section of the student's portfolio of work undertaken.

c. Theoretical Studies

The course includes seventy days of formal tuition on theoretical aspects of conservation, spread over three years as fourteen sessions lasting about one week, when all the students are taught together. Each session takes a particular theme:

- i. Introduction to conservation
- ii. Record-keeping and specifications
- iii. Causes of deterioration and preventative conservation
- iv. Materials Science - metals
- v. Materials Science - wood and other organics
- vi. Conservation materials - metals
- vii. Conservation materials - organics
- viii. Conservation treatments - metals
- ix. Conservation treatments - organics
- x. Industrial archaeology - site work
- xi. Handling and dismantling objects. Working exhibits
- xii. Repair and restoration - metals
- xiii. Repairs and restoration - wood
- xiv. Revision of the foregoing.

As for the practical syllabus, a full description of the theoretical sessions is not appropriate for this paper, but the following example is typical. It is to be understood that unforeseen circumstances might dictate minor departures from this detailed scheme, so it is not to be thought of as rigidly unchangeable.

Materials Science - Metals

Day One

General introduction to history of technology; metals and methods of working them.
Stability and deterioration of metals and alloys.
Practical Work - laboratory examination of structures of metals and corrosion problems.

Day Two

Methods of working metals; their effects on deterioration.
Laboratory examination of worked metals; influence of production-technology on structures of metals.
Spot-tests for identifying metals.
Practical work - identifying metals in the laboratory.

Day Three

Range of metals in industrial collections; manufacturing methods.
Gallery tour - problems in using objects as working exhibits.
Practical work - identification of metals and manufacturing methods; durability.

Day Four

Examination by x-ray, ultrasound; detection of cracks and flaws.
Analysis of corrosion products and surface contaminants.
Demonstrations and practical work on the foregoing.

Day Five

Damage by bad handling - its prevention.
Storage and handling of metal objects.
Packing metal objects.
Introduction to conservation of metals.
Cleaning metals - advantages and disadvantages of various methods.
Protective coatings.
Brief introduction to restoration techniques; joining new metals to originals.

The lecturing and demonstrating is undertaken by members of Science Museum staff and the CICF, and recognized experts in appropriate fields are brought in from outside where necessary. An important element of these sessions is the opportunity to visit other museums and workshops to compare their approach to particular problems. The students also learn thereby something of the latest analytical techniques which are available only to a very few museums or research laboratories.

Assessment

The workplace supervisor provides continuous assessment of the student's progress in practical work on a day-to-day basis, and helps in judging how well the theoretical aspects of the syllabus have been assimilated. In addition, two independent assessors are assigned to each student. As far as possible, one of the examiners is always a conservator, the other an engineer. They visit the student at his workplace three times per year to judge the quality of work undertaken and discuss with the local supervisor what action should be taken if there are any shortcomings.

At the end of each year, all students are examined on their practical work and their understanding of theory. This takes the form of short question-and-answer sessions, both written and oral.

Finally, at the end of the three years, a board of examiners meets to review the results of the examinations, the judgement of the teams of assessors and the quality of the student's portfolio of practical work. If an acceptable standard has been achieved the Certificate in the Conservation of Industrial Collections is awarded.

The course organizers believe that students who have successfully completed this new training course will have the knowledge and experience to meet the particularly demanding challenge of conserving the complex and wide-ranging objects which comprise the ever-growing collections of industrial artefacts.

As the certificate is awarded by the country's premier museum of science, industry and technology (in association with a number of other leading experts in this specialist field), it is expected that it will become widely recognized in the United Kingdom as a major qualification for those employed in conserving such material.

ABSTRACT

This contribution raises the question of whether a restorer of paintings, sculptures and mural paintings requires an artistic and aesthetic training or simply the knowledge of restoration work.

Based on the definition of the art concept, the restorer's task is described, and it is pointed out that the restorer's sensitisation to the "phenomenon of art" is just as essential as his technical training.

ARTISTIC RESTORER OR RESTORATION ENGINEER?

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The American Berenson once said: "A work of art is such a tremendous experience, that, like love, it can't be communicated; you have to experience it yourself."

The true value of a work of art is its "aesthetic". Admittedly every work of art has an historical aspect and consists of various, sometimes extremely valuable materials - but the real motivation behind artistic endeavour is the desire to recall experiences and evoke a response from the viewer. Every work of art is a unique, unrepeatable spiritual expression of the artist.

From the above it is clear that I am limiting my consideration of the term "restorer" to the treatment of works of art, although the profession also includes the preservation of all art and culture - works of art, handicrafts and also utilitarian objects of historical value and those that show the development of manufacturing. That is the first problem. The restorer's job is loosely defined and, because of the high level of specialization, very broad. The term "restorer" (American "conservator") is vague. Even the "The Conservator-Restorer: A Definition of the Profession" issued by the ICOM Committee for Conservation in Copenhagen in 1984 must be treated as a useful guideline rather than a set rule.

Thus the answer to the opening question can only be of interest if we focus on those restorers who work exclusively with fine art. For me, it is a question of whether the technical work, i. e. the achievement in terms of conservation, is of more importance. We know that in the meantime two basic opinions have developed. This is evident in the discontinuation of the former exclusive establishment of conservator training at art academies and the setting-up of relevant departments in some universities or technical colleges. We also cannot get around the fact that in most countries today, the preservation of works of art is distributed among workers from other professions who have picked up conservation knowledge. They have no specialized training and usually no artistic training but they produce valuable work in a specialized field. The profession of restorer is still in its early stages of development.

So, what has become of the liberation of the professional restorer in the last twenty years? The former duo - restorer/art historian - has, for the preservation of monuments, been replaced by the trio - restorer/art historian/architect - and finally in the last fifteen years the scientists have joined us. Alongside this very valuable teamwork there is also a certain degree of suspicion between the individual experts. The cooperation between the various professional groups has resulted in an overlapping of interests. It is disturbing to see how the "quatuor" observes each other and either pushes to take the place of the restorer or feel their own position threatened. Partnerships have not yet been sufficiently clearly defined. The restorer watches uneasily as the otherwise prized scientist sets to work on the object with scalpel and syringe. How can an eye not practised in colour vision or an untrained hand touch up with a fine brush? But also the restorer usually gains only a narrow insight into the type of research, dabbles too readily and opens her/himself to criticism. Admittedly, experience soothes most of the differences. But the role of the restorer as magician's apprentice cannot be overlooked because of the serious question of labour division and the end product. Formerly, only the restorer did the work and was responsible for the result and her/his "art" was more a matter of intuition and skilled craftsmanship. In the meantime it has often been the "spirits" namely the art historians and scientists who guided her/him to success or, as is now no longer uncommon, restored the object themselves.

As I maintained at the beginning, a work of art is the tangible representation of a person's aesthetic activity.

The process of art - the creation of a work of art - is closely linked with the artist's personality, his/her own particular abilities, attitude to life and social ties. Each work of art is a decidedly spiritual creation not a technical one. Thus a work of art achieves a special position as the tangible result of human inventiveness. Consequently, the term "restoration" differs from the term "repair". It is not a question of putting something back into working order, of renovation per se, but it is a task which technology alone cannot accomplish. At the second International Restorer Seminar in Veszprem in 1978, E. van de Wetering indicated in his lecture that the evaluation of materials and the associated aesthetic aspects represent a considerable part of the restorer's work.¹ He also referred to the article by Günter Brandmann on the "Changes in the Evaluation of Materials in the 19th Century".²

This leads us to another important consideration. The awareness of material aesthetics must be attained through knowledge of the effects of the material on the surface and thus on the impressions created by the work of art as a whole.

Each of us knows how many works of art have suffered lasting damage because the restoration measures have changed deliberate surface effects. Among other, I am thinking here of the numerous polychrome wooden sculptures whose azurite gowns were strengthened with beeswax and have now discoloured dark green.

By emphasizing the urgent need for sensitivity and artistic intuition on the part of the restorer, I am not trying to glorify the profession but to create a point of departure for the opening question.

The work of the restorer should perhaps be divided into two fields, even though these are almost inseparable in the end result.

On the one hand we have the problems of technical craftsmanship, i. e. the preservation of the work of art, and on the other we have the aesthetic and intellectual aspect of the object. Every painting restorer's hair stands on end at the thought of processes developed by a group of scientists in a laboratory by which a work of art can be so completely coated in synthetic materials that it is preserved perfectly for centuries. The technical achievement merits praise, but because of the distortion of the original spirit of the work of art, the loss almost outweighs the gain. Today, no restorer can work successfully without the help of the scientist - the decisions which ensure the uniqueness and originality of a work of art demand the trained artistic specialist intuition, the ability to see the slightest nuances of colour, the feel for the spirit of each work of art - the subjective skill this requires can only be gained through years of artistic training, creative work, the discovery of art within oneself. If this side of the restorer's profession were underestimated, the result would be routine technical processes carried out by specialized machinery. A pre-programmed computer could quickly calculate the mean from some given chromatic values, but even a practical suggestion for, say, neutral touching-up would not emerge. Experience and intuition cannot be produced mechanically.

Undoubtedly, the development of a new adhesive, the testing of light-fast varnishes, the analysis of materials etc. is not a matter of artistic flare, but rather an engineering feat on the part of the scientist. This is the clear boundary for the division of labour. Each must recognize the other's field of speciality, and there is no question of substitution.

The restorer must of course play a decisive role in steering research and development. Work on the object continually raises new and valid questions, particularly as regards cooperation with the scientists. Here, the restorer's questions are of prime importance. For me this "partnership" is crucial for the improvement of the quality of our work. While the art historian and the architect work with the restorer with the object in mind, the chemist and the physicist have become indispensable for solving basic problems of our work. Partnership means, though, that neither can take over the work of the specialist.

In the interests of the work of art, I would like to answer the opening question clearly: the restoration engineer is no substitute for the artistic restorer. The scientist is an essential partner, develops whole technologies - but must remain a partner.

I recall here the article by Sheldon Keck in the 1984 "Journal of the American Institute for Conservation" which gives an impressive overall picture.³ In our century, the relationship to a work of art has also been affected by the ubiquity of science. The art historian's search for truth and the restorer's faith in the possibility of working objectively have often encouraged them to go as far as the original surface, which often is no longer available. We should never forget that the value of a work of art lies in its aesthetic fascination which must be preserved.

To put my article into concrete terms, I would like to mention our experience in the artistic training of restorers of paintings, wooden sculptures and murals at the Academy of Fine Arts Dresden. We have long since outgrown the opinion that the best artist, one can always become a restorer. We do not want to turn our students into "restoring artists", and we maintain that without contradicting our opening statement.

Drawing and painting outdoors, learning the basics of anatomy in sculpting, perspective and composition are all preparations for the next stages. Exercises in historical painting techniques are important for touching-up, for restoring missing sections and eventually for copying. The experience of one's own artistic work leads to a sensitive understanding. We want to encourage the ability to empathise so that conflicts between one's own artistic desire and the necessary subjection to the work of art might be avoided.

The results of the last few years have encouraged us in our opinion that only the simultaneous development of artistic intuition and ability with the study of restoration methods leads to an integral view. Technical perfectionism as the restorer's goal is no solution as regards the work of art. This part of the training accounts for about 15 % of the whole five-year course and is particularly concentrated on the first two years.

Training institutes which do not treat the work of art as such and emphasize the technical aspects of restoration do not, in my opinion, do justice to their task.

At this stage the objection that modern works of art are of a different type is often raised. Pieces with engines, technical details, light effects etc. are displayed, and Heinz Althöfer and other restorers have frequently commented on this particular characteristic of current artistic creation.⁴ However, even here, despite the apparent technical aspect of the object, the main issue is the preservation of a work of art, and so aesthetic considerations take priority. We must not overlook the fact that time will select various forms of pseudo-art from the true art. But that is not the restorer's task.

What has been said does not seem particularly controversial. However, if we consider that restoration includes everything from the preservation of a ruin to "more beautiful than ever" reconstruction work, we see it in a different light. The preservation of the object as it was found may be encouraged as maintaining the work's purity; thus any activity on the part of the restorer, however justifiable, was always seen to be interfering, if the overall aesthetic impression was badly distorted. Where this did not happen - and there are enough "whipped" works of art which have been thrown off balance - we are nearer to purely technical achievements than the actual preservation of a work of art. The well-meaning act of restoration distorts more than it saves. The restorer who has never experienced artistic work finds him/herself in the same position as the physically trained acrobat who has to take on the role of the dancer.

So we are back where we started. Considering all adand disadvantages, restoration work on a work of art demands an artistically trained specialist, and despite all the cooperation with art historians and scientists, this cannot be achieved by technology alone. We can only hope that the necessary up-dating of the restorer's profession through science and technology does not lead to a loss of artistic feeling for the piece of art concerned. What damage is caused by doctors who forget their patients during treatment!

Even if this strong emphasis on artistic intuition is a daring venture due to its subjectivity - during training we must try to remain within the bounds of objectivity - but, and I would like to mention this in conclusion, it is the only way to do justice to our works of art as true art.

Reverences:

1. WETERING, E. van de, "Theoretical Consideration with Respect to the completion of Works of Art", (Second International Seminar for Restorers, Veszprem 1978)
2. BRANDMANN, Günter, "Der Wandel der Materialbewertung in der Kunsttheorie des 19. Jahrhunderts", Beiträge zur Theorie der Künste im 19. Jahrhundert, (vol. 1, Frankfurt/M 1971), 129 - 157
3. KECK, Sheldon, "Some Picture Cleaning Controversies Past and Present", Journal of the American Institute for Conservation, 2 (1984), 73
4. ALTHÜFER, Heinz, "Moderne Kunst. Handbuch der Konservierung" (Düsseldorf 1980)

ABSTRACT

This paper describes a two-day open examination, one of the assessment techniques used since 1980 for students on the Three Year Postgraduate Diploma Course in Textile Conservation, run by the Textile Conservation Centre in conjunction with the Courtauld Institute of Art, London. A brief description of the history and content of the Diploma Course precedes a detailed description of the open examination. Each student has two days to inspect a historic textile requiring conservation treatment and to prepare a detailed written report, which is the basis for a subsequent via-voce examination. The effectiveness of the open examination as an assessment technique is considered.

KEYWORDS

Textile Conservation
Training
Student Assessment
Examinations

DEVELOPING STUDENT ASSESSMENT TECHNIQUES IN CONSERVATION TRAINING

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INTRODUCTION

The development of structured conservation training courses has led to the development of techniques to monitor and assess the progress of conservation students. This paper concerns one of the assessment techniques developed for the Three Year Postgraduate Diploma Course in Textile conservation run by the Textile Conservation Centre in conjunction with the Courtauld Institute of Art, University of London.

A brief outline of the history and content of the Diploma Course introduces the main topic of this paper, a two-day open examination, set at the end of the second year of the three year course. A detailed description of the examination is followed by an assessment of its effectiveness.

THE DEVELOPMENT OF THE DIPLOMA COURSE

The development of the Three Year Postgraduate Diploma Course in Textile Conservation is closely linked to the development of the Textile Conservation Centre. The Centre was established in 1975 by Karen Finch OBE, a pioneer of conservation training. Even before the Textile Conservation Centre was established Karen Finch had close links with the Courtauld Institute of Art and from 1973 two pilot courses (each of two years' duration) were held before the Three Year Diploma Course was started in 1978. The training was extended from two to three years' duration to increase the variety and range of the students' practical conservation experience.

In the first year of the Diploma Course students study the factors which result in the deterioration of textiles - inherent factors such as the chemistry and technology of fibres, dyes and finishes and environmental factors such as storage and display conditions. In the second year students undertake a wide variety of remedial conservation projects. In the third year each student undertakes a major conservation project, chosen for its research interest.

Karen Finch stressed the importance of developing teaching and assessment methods that would produce professional textile conservators able to take up positions within museums and other institutions. It is her work and the work of all those who have been involved with teaching at the Centre over the years, which has produced the Diploma Course in its present form and which has laid the foundations for the present assessment structures.

The Aims and Assessment of the Second Year

The second year of the Diploma Course builds on the work of the first year in the areas of practical conservation and science and technology, by placing the emphasis firmly on practical conservation. To this end, the second year students work on a wide range of client-owned objects, guided in their approach by the conservator tutors. The students are expected to develop their abilities to assess the methods of scientific analysis and conservation techniques available to them. In addition, full documentation of their work must be provided.

The work of each second year student is assessed within the framework of continuous assessment laid out in the Diploma Course structure. The second year students must pass five units of course work:-

1. Practical conservation work as carried out on client-owned objects - 1 unit.
2. Documentation of practical work - 1 unit.
3. Verbal presentation of conservation work during discussion sessions and seminars - 1 unit.
4. Theoretical and scientific aspects of practical work and seminar assignments - 1 unit.
5. The second year open examination - 1 unit.

The open examination forms an important part of the student's assessment.

The Open Examination

The open examination, which was introduced in 1980, consists of a two-day examination followed by a viva-voce examination. The title 'open' has been chosen because the students have at their disposal all the resources of the Textile Conservation Centre to aid them during the two-day examination. This means that the laboratory and library facilities are readily accessible to them for research and analysis.

At the commencement of the two days the students are given written instructions about the examination procedures. Each student is then allotted an object or small group of objects, accompanied by a written brief outlining some background information on the client's requirements. The student is asked to inspect the object and document the object and formulate proposals for its conservation treatment. In documenting the object the student is expected to identify the materials present and to show s/he has considered the ethical and practical problems of any destructive analytical techniques employed. A written report is prepared by the student and submitted for consideration by the examiners. Although full documentation will normally include detailed photography, this is not undertaken as part of the open examination.

This two-day examination is followed by a viva-voce examination, in which the student presents his or her findings to the examiners. During the viva both the student and the examiners have the opportunity to clarify any points that were unclear or to add information that was omitted from the report. The viva-voce examination lasts approximately 30 minutes.

The objects selected for the open examination in 1988 (when eight students were examined) are listed by way of illustration:

Two 17th century embroidered panels

Five Pre-Columbian fragments.

A 19th century painted banner

A beadle's uniform

A Egyptian garment from an archaeological context

A knotted pile rug

An early 19th century dress

A document printed on fabric.

This selection of objects was felt to be representative of objects encountered by students during the year, although they had never seen these particular pieces before.

Two workrooms were set aside for the students, who were provided with table space for examining the objects, stereo microscopes and equipment for carrying out certain basic analytical tests such as for dye fastness and the measurement of pH.

Within the laboratory chemicals and reagents for micro-chemical analysis were prepared in advance so that they were readily available for use by the students. The practical difficulties of ensuring that each student had sufficient time in the laboratory during the two-day examination was overcome by drawing up a timetable for use of the laboratory and microscopes.

As mentioned earlier each student was supplied with a written brief, giving background information as to the ownership of the object and client's requirements. The aim of the brief is to guide the student to consider the problems of an object within a 'real' context, and to help the student to make realistic proposals tailored to the specific needs of the object and the client.

Objects Selected for the Open Examination

At this point it may be useful to consider the objects selected in 1988 more closely to gain insight into aspects that the students were expected to emphasise in their reports.

17th century panels - These were heavily encrusted with an adhesive which had stiffened the textile considerably. The client brief stated that the owner, a private individual, would like the pieces cleaned and mounted for display within their home. Therefore the student's main aim, after a full description of the object and analysis of the materials involved, was to identify the adhesive and to propose methods for its safe removal. Removal of the adhesive would increase the flexibility

of the textile, enabling it to be mounted for display.

The student would also be expected to consider the possibility that the adhesive could not be totally removed and suggest alternative methods of mounting. The student would also be required to make recommendations for the safe display of the object within the uncontrolled environment of a private house.

Five Pre-Columbian Fragments - The client brief directs the student towards the consideration of treating the collection as a whole in order to present the group as a unified and transportable study collection, used by a private individual for teaching purposes.

19th Century Painted Banner - This object displayed many problems associated with poor storage conditions, such as fungal growth, water staining, delamination of the paint layers etc. The student was expected to consider the safest methods of cleaning and supporting a painted textile. In this case, the student would be expected to assess the advantages and disadvantages of a stitched support and an adhesive support.

Beadle's Uniform - The uniform comprised two costume items which required cleaning and structural support. The student would need to consider the practicalities of aqueous as opposed to solvent cleaning and how to mount these three-dimensional objects for safe display within an uncontrolled environment.

Egyptian Garment from an Archaeological Site - The archaeological context of this garment makes it an important document and the student would be required to consider all the possible options for analysis. In order to glean as much information as possible from the object, the proposed conservation treatments should entail minimum intervention. The fact that it is owned by a museum would suggest that the student could make recommendations for environmental control and monitoring.

Rug with Pile - The student should consider that private clients often seek a more 'restorative' approach to treating rugs. The problems of restoration versus conservation should be discussed, together with the problems of treating an object with a pile. Methods of minimising wear of rugs that are to be used after conservation should be mentioned.

19th Century Dress - The dress was soiled and in pieces, therefore suggestions on the cleaning and re-assembly of the dress were required together with ideas for a mounting system that would allow the dress to be used for study purposes.

A Document Printed on Silk - This piece was adhered to the back of an old photograph, making its removal an ethical dilemma. The student would be expected to address the possibility that the piece could be damaged if removal were attempted and that an alternative, non-interventionist approach should be considered alongside possible removal techniques.

Marking the Open Examination: Report and Viva-Voce

Documentation methods taught at the Textile Conservation Centre throughout the first and second years stress the importance of producing comprehensive reports, starting with a full description and technical analysis of the object to include fibre and weave analysis. This should be followed by a complete condition report for all components of the object. Only when all this information has been gathered, can proposals for conservation treatment be made. Finally, estimates for the length of time that treatment options will take and recommendations for storage and display are given. The students were expected to follow the same format during the examination and each student is assessed on his or her ability to:-

1. make an accurate assessment of the object's condition and a careful evaluation of treatment options
2. present a clear, well-written and well-organised report, including time estimates (for every stage of further analysis and the treatment options proposed)
3. make a clear verbal presentation and answer the examiners' questions.

Once the reports have been handed in at the end of the examination period, the examiners meet to examine the objects thoroughly and through discussion, decide what they are looking for in each report. Only when the examiners have thoroughly examined the objects, do they read the students' reports. The examiners can spend up to four days on this work: one day to examine the objects and about three days to read the reports thoroughly, making notes of strengths and weaknesses as a basis for questions to be asked during the viva.

If it is felt that the student has misinterpreted test results, these

are checked by the examiners at this stage.

Examiners are appointed by the Diploma Course Board of Studies, with each examiner being assigned a clear responsibility. Three examiners are appointed for the open examination: two internal examiners and one external examiner. The internal examiners are drawn from the Diploma Course tutors. The second year tutor and the science tutor are normally assigned to the open examination. The external examiner is chosen from another institution and he or she may be a conservator, a conservation teacher or a textile curator.

Before the vivas, the internal examiners assign marks for the report. The second year tutor and the external examiner then conduct the viva and use it to make any adjustment to the marks that are warranted by the students' oral presentation during the viva-voce part of the examination. The external examiner takes the more active role in the viva, while the internal examiner, who knows the student well, take a supporting role and tries to put the student at ease. When the marks have reached their final adjustment through discussion between the examiners, they are presented to the Board of Studies for its approval.

Assessing the Value of the Open Examination

The main question that has to be asked when considering the suitability of this type of examination is, does the student's performance during the examination reflect the student's ability and performance throughout the year (as shown in continuous assessment).

In our experience, this examination seems to reflect very accurately the student's performance across the range of their second year course work. Obviously, it cannot test practical conservation skills, which have to be assessed in other ways, but in part it does show the student's ability to document an object and propose treatments. It will show whether the student can think creatively about treatment proposals and solve questions with a degree of flexibility. It also tests the student's ability to select relevant analytical tests and to make best use of available resources in the limited time available for the examination. It tests the student's powers of observation and the degree to which the student has assimilated different approaches to conservation problems.

Students themselves have commented that the open examination is a useful and positive experience, which helps them to concentrate on what they have learned during the year.

However, problems can arise. A student's performance can be affected by inadequate briefing as to what is expected from them in this examination. Therefore briefing must be thorough and should aim to emphasise that, since there is a time limit, the student has to make intelligent choices about what to include or omit from their report rather than trying to include all that they have learned during the year.

On a practical note, this examination works well with a small group of students, where adequate resources can be made available, e.g. examiners; time; workroom space; laboratory facilities etc. At the Textile Conservation is closely linked to the development of the Textile of 4-8 students. The staff time commitment in the open examination is considerable.

Conclusion

In developing structured conservation training it is necessary to develop appropriate assessment techniques. Students on the Three Year Postgraduate Diploma Course in Textile Conservation are assessed in a variety of ways, ranging from continuous assessment to formal written examination. The two-day open examination has been developed to assess an important range of skills:

- observation and documentation
- analysis of materials and techniques
- assessment of condition
- evaluation of treatment options
- oral and written presentations.

Since its introduction in 1980 the open examination has proved to be an effective method of assessing textile conservation students at the Textile Conservation Centre.

ABSTRACT

For a long time the most usual way of training restorers in the USSR appeared to be through a system of individual tutorship in the large restoration centers under the guidance of qualified experts. Now the training of restorers at the USSR is organised in the state colleges and professional schools. A particular feature of the Soviet state system of educating restorers consists of professional recognition for the specialist. Within the system of training restorers special groups study is organised at large regional museums, restoration facilities or archaeological expeditions. Today the Soviet system of education for restorers and for qualification improvement undergoes the process of further development and sophistication.

KEYWORDS

Training of restorers, qualification "artist-restorer", restoration and storage of painting, museums, recognition at the category.

PROBLEMS OF EDUCATING RESTORERS IN THE USSR

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Introduction

The Soviet state has always paid proper attention to the preservation of historical and artistic monuments. An important place in this process, sanctified by the State Law "On the protection and usage of historical and cultural monuments", belongs to Soviet restorers.

The particular importance of training restorers in our country follows from the abundance of artistically and historically valuable pieces of art which urgently require restoration. Even before the Second World War disparate attempts were undertaken to organise a systematic professional training of restorers on the basis of modern scientific standards, mainly at some large museums. But really tangible and stable results were achieved only during two last decades.

For a long time the most usual way of training restorers in the USSR appeared to be through a system of individual tutorship in the large restoration centres under the guidance of qualified experts. Along with many advantages it has a number of shortcomings. First of all this process was not able to provide the necessary number of apprentices as well as giving them a reasonably high level of scientific and theoretical knowledge.

Now the training of restorers at the USSR is organised in the state colleges and professional schools.

Training of restorers

In the educational system at the level of professional schools, beginning from 1966 a continual training of restorers has been carried out at the Moscow Artistic School of the Memory of the 1905th year, with specialisations in restoration of oil easel paintings, tempera easel and monumental paintings. The second such educational facility is the Leningrad Artistic School under V.Serov, with specialisations in restoration of oil paintings, tempera easel painting and of graphic works. The state registration number of specialities in both of these schools is 2134 under the condensed nomenclature "Restoration and storage of paintings". The period of apprenticeship amounts to three years and ten months. The special courses comprise 1652 hours of lecturing. The graduates acquire the qualification "artist-restorer". The usual number for every year amounts to 9-10 persons at each school.

In 1973 the specialised artistic school at Suzdal was organised. The first graduation from it occurred in 1983 with specialisation in restoration and storage of oil and tempera paintings. In 1984 for the first time specialists in the field of restoration of metal art-works graduated from the school.

Today at the Russian Ministry of culture the issue of the organisation of professional branches engaged in training of specialists for the RSFSR restoration facilities at Moscow, Leningrad, Vladimir, Novgorod, Pskov, Tomsk has been decided. But it should be taken into account that the main direction of their development is oriented to the needs of architectural restoration. The same development can be observed now in other Soviet republics. An example of it can be shown by the activity of the Tbilisi professional and technical school.

The system of higher education in this field is represented in our country by four colleges. In 1969 there was established the restoration branch at the Kiev state art institute with specialisations in oil easel, tempera easel and monumental decorative paintings. In 1970 a similar branch was opened at the Georgian Art Academy with specialisations in oil easel and monumental paintings; in 1971 at the Leningrad Institute of painting, sculpture and architecture under I.E.Repin with specialisations in oil easel and tempera easel paintings. For these colleges the educational plan with the state registration number 2219 was approved, under the name "restoration of easel and monumental decorative paintings". In May 1976 the USSR Ministry of higher and special education approved the thematic plan for

training restorers which was prepared at the Institute by I.E.Repin and later sent to all educational facilities where restorers are taught. The basic studies according to that plan require 800 hours. A yearly graduation per facility is about 5-10 persons. The graduates obtain a qualification, "artist-restorer".

In 1983 the first apprentices commenced studying the restoration of monumental decorative paintings at the Moscow Higher artistic and industrial school (formerly Stroganoff's).

This current system of higher and special education, described above, involves a set of problems due to the specificity of restoration activities, because it demands a very complex and multifaceted form of training. Here it is first necessary to teach more students, then the development of special text-books and programs, as well as a widening of the circle of teachers and of technical possibilities for practical studies.

Since the training of restorers at any type of educational facility has not yet been up to standard connected with a scientific competence and a wide professional interest in serving restorers, it is necessary to develop and modify the system of qualification improvement. Now, this system is built on the basis of new methodic principles in the field of protection and restoration of historical and artistic monuments.

In general outline, the system of qualification improvement resembles somehow a pyramid with a foundation of local museum restoration services and analogous establishments under regional directions in some research institutes, particularly archaeological and ethnographical ones, in archives and so on. The upper point of this pyramid is constituted by the All Union Research Institute for Restoration (VNIIR) and the All Union Institute of Qualification Improvement, both of the USSR Ministry of culture. These two establishments develop themes for studies to be established, plan the duration and places of study, compile scientific and methodic materials, organise groups to be taught and look after all necessary documentary formalities after completion of studies. Depending upon the level of preliminary study the objects for restoration treatment by students can be taken from the so called experimental collection or directly from museum collections.

A particular feature of the Soviet state system of educating restorers consists of professional recognition for the specialist. According to its rules the special state commission determines the level of the present qualification for each applicant. There are four grades of professional recognition and for each such grade the applicant is obliged to display a definite level of professional ability, of knowledge and experience, of proper discrimination concerning responsibilities and duties, from the simplest to the most complicated at the highest grade. The lowest grade, which is called the third category, can be provided for these persons that served in the field of restoration for not less than three years, have accumulated some initial experience and have the ability to carry out simple operations. Such persons nevertheless are not allowed to work independently but only under supervision of skilled experts. Only those who were awarded the level of the following second category can be authorised to execute some simple operations on their own. For them it is required that they serve about six or seven years. Only the most experienced and reliable specialists have the right to demand recognition at the first category, and still rarer to the highest qualification. Usually it requires more than ten years of flawless service. Depending upon his real level of expertise a restorer is allowed to carry out this or that practical work with direct consequences as to his payment. Therefore, novices are stimulated to increase their skills and knowledge, enlarge their experience and get in touch with the newest methods and materials.

Within the system of qualification improvement, special courses for practicing restorers and college or technical school graduates, are organised with the view to prepare them for advancement to the third category during three or four years. The corresponding program in such a case closely follows the qualification characteristics for the third category. Another program is developed for qualified restorers so as to help them to study for the nearest next category according to their professional growth.

As a very useful measure it is commended that specialised groups study at large regional museums, restoration facilities or archaeological expeditions. For example, such studies were regularly carried out at the Cyrillo-Bielozersky art historical museum of the Vologda region, at the restoration shop "Kazmuseum-restoration" of the Kazakh Republic, at the museum "Olvia" of the Nicolaev region of the Ukrainian SSR, at the museum "Metzamor" of the Armenian Republic and so on. During such "outdoor" studies the students get closer to the new experience of local artistic material and of its restoration treatments, then, secondly, they help considerably to repair damaged objects from local museum collections.

Also of considerable interest is a related but inversed form of regional participation. In this case skilled experts go to local museums and restoration establishments and instruct related personnel. As an example can be mentioned an annual training for Ukrainian restorers at the specialised restoration shop of the Ukrainian Ministry of culture, and another one for Transcaucasian colleagues, who serve in the field of applied art restoration at the Abkhazian museum of local history.

In addition to restorers who have their respective individual study programs, there are also museum curators, biologists, chemistry and physics specialists, climatologists, light technicians and the like.

After the studies the participants obtain certificates on the character and amount of received knowledge, with exact specifications as to the type of operations permitted for autonomous execution. In addition every student is given a particular educational task for the future requiring one or one and a half years, in order to better his or her standard before commencing the next round of qualification improvement.

The restorers of the highest qualification, starting from 1982 at VNIIR have organised annual all union scientific seminars with the aim of exchanging experiences. It is a new and promising way of education. These seminars have the general name "New methods of examination, conservation, restoration and storage of museum valuables". Each year the organisers of the seminar choose some definite urgently needed theme, which will undergo common discussion by the best specialists in the respective field.

The first such seminar was held at Moscow in 1982, which involved the most immediate problems of restoration. Among them the participants singled out the necessity to develop criteria of operational complexity in restoration, then to determine a number of first rate monuments for immediate conservation and restoration, and as a follow-up, to develop a far ranging plan of conservation and restoration for all kinds of art. The extremely important question of the juridical responsibility of the restorer was also hotly discussed, following which it was decided to prepare a publication on this question as well as another one on the obligation to satisfy all storage regulations. At the seminar, also considered were the necessities of supplying material for restoration facilities, and some possibilities to promote rationalisation and research in the field of restoration and so on.

The next two seminars were devoted to problems of current restoration practice. In 1983 at Moscow the seminar discussed applied art restoration (textiles, metal, glass, ceramics, stone). Many reports contained descriptions of new restoration methods, of new materials, of new examination procedures together with comments on the restoration of the most widely known artistic and historical monuments.

The next seminar of 1984 was held at Kiev on the problems of investigation, conservation and restoration of archaeological objects. The participants considered the history of this particular field of restoration, and the most recent methods of chemical and optical analyses for restoration purposes. Also discussed were developments in new working methods and results of field and laboratory treatments of recent cases of restoration of unique findings.

During recent years, VNIIR has developed the practice of training foreign restorers and specialists. In the course of three years at the Institute, colleagues from Bulgaria, DDR, Vietnam, Kampuchea, Yugoslavia, Cuba, Spain, Holland, USA and France had their opportunity to improve restoration and scientific stan-

dards. They got acquainted with new restoration processes, and respectively used materials in the sections dealing with oil easel paintings, tempera easel paintings, monumental paintings and applied art, at the research laboratories.

Conclusion

Today the Soviet system of education for restorers and for qualification improvement undergoes the process of further development and sophistication. Its main tasks are the same as before. First of all it is necessary to enlarge the quantity of restoration personnel in the country; next to develop educational and methodical publications; then to organise courses for new specialisations so that not only paintings restorers are trained, but also restorers in every possible kind of art, for example, in sculpture, in graphics, in archaeological and ethnographic materials. Some new far reaching plans for a considerable broadening of the education of restorers in the USSR are now in the state of preparation.



Working Group 22

Metals

Métaux



RESUME

Le présent rapport offre les résultats de l'étude des compositions chimiques d'alliages de fonderie d'une série d'oeuvres plastiques monumentales. Des éprouvettes appropriées ont été mises aux essais dans des conditions atmosphériques et dans des conditions de corrosion accélérée en vue de déterminer les propriétés du cuivre, des laitons simples et multicomposants et des bronzes. On a établi une dépendance de la composition des phases, de la structure et des propriétés décoratives et de protection des patines en fonction de la teneur des alliages en éléments d'addition.

MOTS-CLEFS

Corrosion, alliages de cuivre, composition, propriétés, microstructure, patine

Tableau 1

Microstructure des alliages de cuivre, utilisés pour la fonderie, X 70:



Bronze 2,8 % Sn

ALLIAGES DE CUIVRE EN FONDERIE D'ART. ETUDE EN MATIERE DE CORROSION

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Introduction

Une des tâches principales lors des modelage et restauration de la sculpture monumentale consiste à faire un bon choix d'alliages et de revêtements décoratifs et de protection, choix qui prennent considération des conditions futures dans lesquelles tel ou tel autre monument sera utilisé. Les facteurs agressifs de l'atmosphère exercent une influence néfaste sur la surface de monuments réalisés en alliages de cuivre. Une patine naturelle se forme sur la surface desdits monuments à la suite de la corrosion atmosphérique. Une analyse comparative des patines formées dans diverses conditions atmosphériques démontre que celles-ci diffèrent par leurs compositions des phases, leurs couleurs et par d'autres caractéristiques. Certaines publications affirment que les qualités décoratives des patines sont fonction de la composition d'un alliage utilisé. Cependant cet aspect du problème n'est pas encore bien étudié.

Il existe peu de renseignements sur les compositions chimiques d'alliages de cuivre utilisées dans la fonderie d'art.

Les recherches effectuées dans le domaine de la sculpture de grandes et de petites dimensions prouvent que pour son modelage outre les bronzes on a aussi souvent utilisé des alliages qui, d'après leur composition, peuvent être rapportés aux alliages à base de cuivre et de zinc, l'étain et le plomb servant d'éléments d'addition (1-4). Le tableau 1 offre les données sur la composition chimique des alliages de cuivre qu'on a utilisé pour la fonderie de quelques oeuvres monumentales.

On s'est donc proposé d'étudier les particularités de formation de patines sur divers alliages de cuivre utilisés dans la fonderie d'art et, notamment, cela concernait les bronzes à l'étain et divers laitons.

On a réalisé toute une série de travaux visant à déterminer de quelle façon les éléments d'addition des alliages en question exercent leur influence sur la composition, la structure et les propriétés décoratives de patines naturelles. Des compositions suivantes ont été choisies pour les études en matière de corrosion: cuivre, bronzes à l'étain où la teneur en étain variait de 3 à 11%, laitons simples et multicomposants où la teneur en zinc variait de 3 à 33%, en étain, de 3 à 8%, et en plomb, de 1 à 6%.

On faisait des éprouvettes par moulage en argile et sable à vert. La fabrication des alliages se produisait dans un four à induction ouvert du type MCT-006. A titre de flux de couverte on utilisait le charbon de bois. Dans tous les cas la surchauffe du métal constituait de 100 à 120°C au dessus de la ligne du liquidus en fonction de la composition d'un alliage. La coulée dans les moules se faisait à une température de 50°C au dessus de la ligne du liquidus.

Les essais de corrosion accélérée comparatifs ont été effectués dans les chambres "Feutron" à H=100%, T=40°C et dans les chambres qui ont imité une atmosphère industrielle à H=95%, T=40°C et $C_{SO_2} = 5 \text{ mg/m}^3$.

On a aussi fait des essais naturels sur un banc durant sept ans dans les conditions de Moscou.

La corrosion a été déterminée d'après le changement du poids tout en gardant les produits de celle-là.

L'étude de la composition des phases et de la structure des alliages se faisait à l'aide des méthodes suivantes: métallographique, électro-microscopique, microradiospectrale et structurale à rayons X.

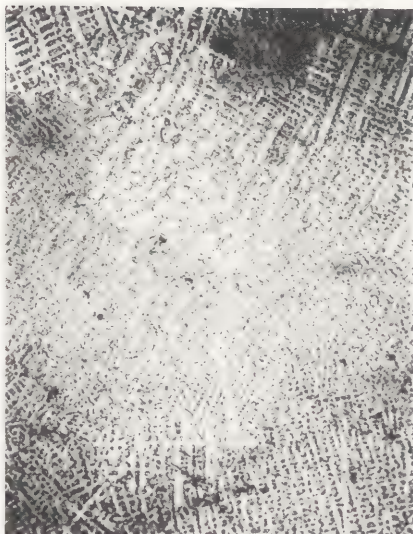
Les essais effectués ont démontré que la corrosion des alliages de cuivre utilisés dans la fonderie d'art a un caractère régulier, qu'elle s'affaiblit avec le temps et qu'elle s'accompagne

b)



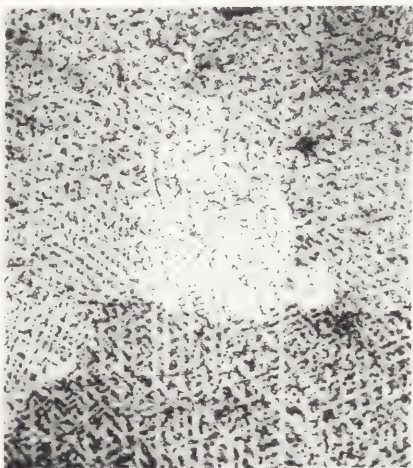
Bronze 7,1 % Sn

c)



Laiton (7,3% Zn, 7,3% Sn, 3% Pb).

d)



Laiton (14%Zn, 6,3% Sn, 1% Pb)

par une formation de couches protectrices. La résistance corrosive des alliages est déterminée par leur composition et leur structure. On a établi que les alliages étudiés peuvent être disposés, d'après la diminution de leur résistance à la corrosion, dans l'ordre qui suit: Bronzes à l'étain, cuivre, laitons (de 3 à 7% de zinc, de 3 à 7% d'étain, de 1 à 6% de plomb), laitons (3 à 10% de zinc), laitons (de 7 à 14% de zinc, de 3 à 7% d'étain, de 1 à 6% de plomb), laitons (de 12 à 15% de zinc), laitons (de 20 à 35% de zinc).

Ainsi on a constaté que les bronzes à l'étain, le cuivre, les laitons simples et multicomposants (contenant jusqu'à 10% de zinc) sont les alliages les plus résistants à la corrosion dans les conditions de l'atmosphère industrielle.

Le facteur structural est un des facteurs qui déterminent la résistance à la corrosion. Avec l'augmentation de la teneur en éléments d'addition tels que l'étain, le zinc et le plomb, on observe dans la structure des alliages un renforcement de l'inhomogénéité dendritique α de la solution cristallisée, une apparition des phases eutectoïdiques δ ($\alpha + \text{Cu}_3\text{Sn}$), SnO_2 et des sphéroïdes du plomb (Microstructures de certains alliages de cuivre, utilisés pour la fonderie, étudiés dans ce rapport sont représentées sur le tableau 1). L'augmentation de la teneur en zinc dans lesdits alliages conduit à une réduction de la résistance à la corrosion ce qui est dû à un processus chimique, plus précisément à la dissolution anodique du zinc conduisant à la dézincification.

On a étudié les produits de corrosion qui se sont formés sur le cuivre, les bronzes et laitons dans de différents milieux corrosifs. L'étude des patines a démontré que leurs qualités décoratives - couleur, régularité, continuité, homogénéité, facture etc.- sont fonction non seulement de la composition atmosphérique, mais aussi de la composition des alliages eux-mêmes (des microstructures typiques des patines formées sur les bronzes et laitons dans les conditions identiques de corrosion sont représentées sur le tableau 2). Des patines régulières, continues, denses et adhérent bien à leurs supports se forment sur le cuivre, les bronzes à l'étain et les laitons contenant jusqu'à 15% de zinc. Si la contenance en zinc est supérieure à 15%, la patine devient irrégulière et friable. La gamme de couleurs des patines monocouches varie durant le processus de corrosion: pour le cuivre du brun jusqu'à la couleur de chocolat, pour les bronzes à l'étain du brun jusqu'au brun foncé et pour les laitons, du jaune-brunâtre jusqu'au noir.

La gamme chromatique des patines bicouches varie de la façon suivante: pour le cuivre, du noir jusqu'au vert foncé, pour les bronzes à l'étain, du noir jusqu'à la couleur d'olive bleue et de malachite, pour les laitons, du noir jusqu'au bleu et vert foncé.

L'étude de la composition et de la structure des produits de la corrosion a été faite à l'aide d'un analyseur microradiospectroscopique JSM. A cet effet on a utilisé 35 méthodes d'un faisceau glissant des rayons X et la méthode de Debye-Scherrer. Les données obtenues ont permis de constater les particularités de changement de la structure et de la composition des phases des patines durant les essais de corrosion. La méthode d'un faisceau glissant des rayons X présente un intérêt particulier pour l'étude de formation des patines. L'avantage de cette méthode consiste en ce qu'on peut poursuivre les recherches à même la surface d'une patine en laissant saine et sauve sa structure. Cette méthode permet de réaliser, couche par couche, l'analyse des phases de la composition et des particularités structurales des patines sans aucun traitement supplémentaire de ces dernières et, pratiquement, à n'importe quelle rugosité superficielle.

La méthode de faisceau glissant est une variation de la radiographie des matières polycristallines qui se fait au moyen d'une chambre à rayons X standard. La différence de ladite méthode consiste en ce que le dispositif de la chambre à rayons X permet de réaliser la radiographie sous un petit angle qui se forme entre la direction des rayons X et une éprouve qu'on étudie (5).

A l'aide de la méthode du faisceau glissant des rayons X on a déterminé la composition des phases des patines (des exemples d'analyse des phases couche par couche et la répartition des phases selon la profondeur de la patine, obtenus à l'aide d'un faisceau glissant des rayons X sont représentés sur les tableaux 3-4). On a constaté qu'outre les combinaisons détectées avant, cuivre-cuprite, brochantite, azurite, malachite - les patines comprenaient en petites quantités les phases des oxydes telles que

e)



Laiton (34,7% Zn, 3% Sn,
2% Pb, 0,92% Fe, 0,73%
Al, 0,37% Sb).

Tableau 2

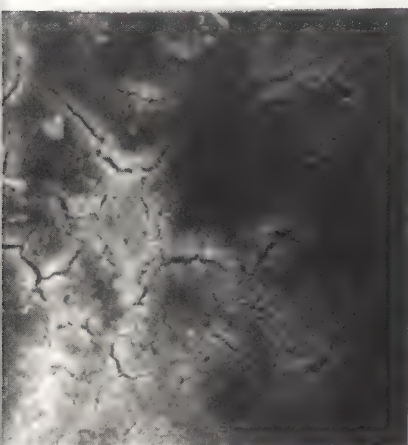
Microstructure de la sur-
face des patines, formées
sur les alliages de cuivre
utilisés pour la fonderie
à H=95%, T=40°C,
C_{SO₂} = 5 mg/m³ après 180
jours.

a)



Bronze (2,8% Sn)

b)



Bronze (7,1% Sn)

CuO; Cu₂O·6 CuO; Cu_{2-2n}O; ZnO; SnO, les phases des sels telles que CuSO₄·CuO; (Cu,Zn)₅CO₃(OH)₆; (Cu,Zn)₂CO₃(OH)₂; CuSO₄·nH₂O et composés isomorphes CuSO₄-ZnSO₄.

La plupart de ces minéraux se rapportent selon leurs structures cristallines, aux singonies monoclinique et triclinique et sont caractérisées par des compositions qui varient. Cela concerne les patines qui se sont formées sur des alliages dont la teneur en étain est supérieure à 5,0% et en zinc, supérieure à 7,0%.

On a détecté dans plusieurs minéraux des patines des substitutions isomorphes et hétérogènes des ions d'étain et de zinc.

On a déterminé que le constituant principal de structure de la patine se trouvait en état cristallin. Les impuretés du constituant principal de structure avaient soit une constitution cristalline dissimulée, soit une constitution de fine dispersion. A noter que le nombre d'impuretés finement dispersées augmente dans le sens allant de la surface intérieure vers celle extérieure de chaque couche qu'on étudie. Cela prouve que la croissance de pellicule de protection naturelle est régie par le mécanisme de diffusion.

Conclusion

Les recherches effectuées ont permis d'établir la dépendance de la composition des phases et de la structure des patines en fonction de la teneur des bronzes et des laitons en éléments d'addition. On a révélé une augmentation des paramètres du réseau des oxydes de cuivre faisant partie de la patine qui s'est formée sur les alliages où le teneur en étain est supérieure à 5% et en zinc, supérieure à 7%. La répartition de l'étain et du zinc dans la patine est fonction de la composition et la structure d'un alliage donné. Les microportions de patine riches en étain sont rapprochées des espaces interaxiaux des dendrites et des inclusions eutectoïdiques. Quant au zinc, il est réparti dans les produits de la corrosion d'une manière plus régulière. Si dans un alliage quelconque la teneur en zinc est supérieure à 15%, il se produit une augmentation de la contenance des phases de zinc dans la patine. Ceci conduit à une réduction des propriétés décoratives et de protection des patines.

Ainsi, les études de corrosion effectuées avec des alliages de cuivre utilisés dans la fonderie d'art ont démontré que la composition des phases, la structure et les propriétés décoratives et de protection de patines sont en rapport direct avec la contenance en éléments d'addition. Il est nécessaire de le prendre en considération lorsqu'il s'agit du choix d'un alliage à des fins d'un modelage ou d'une restauration d'une oeuvre de la sculpture monumentale.

Bibliographie

1. Rotatch A.L. Colonne d'Alexandre.-L. Stroïzdat, 1966, p.80.
2. Restauration du monument à Pierre le Grand (Statue équestre) de E.Falconet. (Compte rendu) Groupement de recherche-production spécial "Restavrator". L., 1976, p.54
3. Etude avec élaboration d'une méthode de procédés technologiques de restauration du monument "Millénaire de la Russie" dans la ville de Novgorod. (Compte-rendu). LOSNRPM, 1., 1982, p.51
4. Restauration du monument à Catherine II, oeuvre de M.O.Mikéchine, A.M.Opékouchine et M.A.Tchijov. (Compte-rendu). Groupement de recherche-production spécial "Restavrator". L., 1979, p.75
5. Rybakova L.M., Kouksenova L.I. Structure et résistance à l'usure des métaux., M., Métallurgie, 1982, p.212.

c)



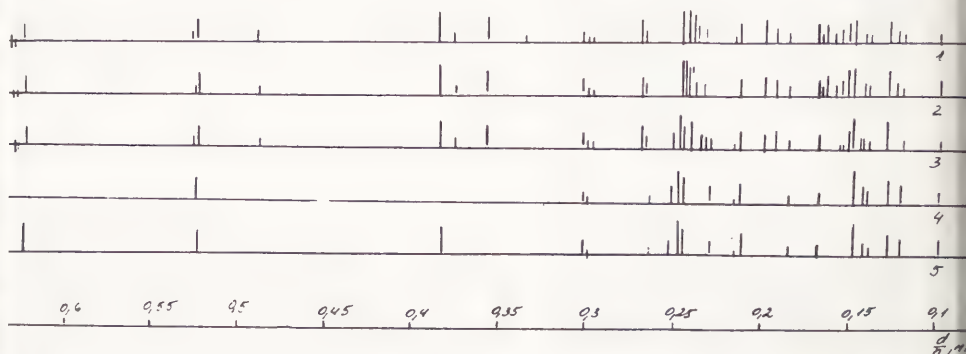
Laiton (7,3% Zn, 7,3% Sn, 3% Pb).

d)



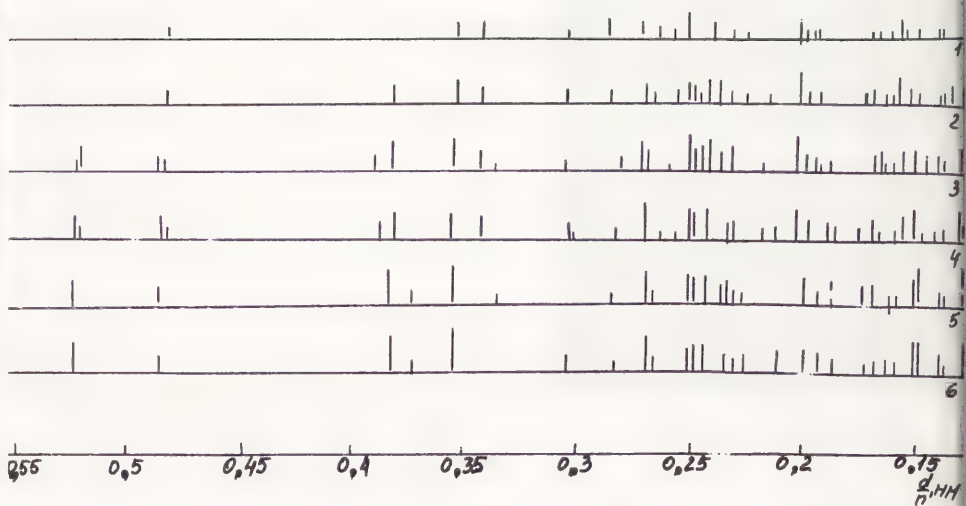
Laiton (14% Zn, 6,3% Sn, 1% Pb).

Tableau 3 Répartition des phases selon la profondeur de la patine, formée sur bronze (7,1% Sn) à H=95%, T=40°C, C SO₂ = 5 mg/m³ après 180 jours. Résultats obtenus à l'aide d'un faisceau glissant des rayons X:



- 1) = 1° Cu₂O, CuSO₄·3 Cu(OH)₂, CuSO₄·3 Cu(OH)₂·H₂O
- 2) = 2° Cu₂O, CuSO₄·3 Cu(OH)₂, CuSO₄·3 Cu(OH)₂·H₂O
- 3) = 4° Cu₂O, CuO, CuSO₄·3 Cu(OH)₂·H₂O
- 4) = 6° CuO, CuSO₄, CuSO₄·3 Cu(OH)₂
- 5) = 10° Cu₂O, CuO, CuSO₄·3 Cu(OH)₂

Tableau 4 Répartition des phases selon la profondeur de la patine, formée sur laiton (14% Zn; 6,3% Sn; 1% Pb, le reste -Cu) à H=95%, T=40°C, C SO₂ = 5 mg/m³ après 180 jours.



- 1) = 30' ZnSO₄·H₂O, ZnO, CuSO₄·3 Cu(OH)₂·H₂O
- 2) = 1° ZnSO₄·H₂O, ZnO, CuSO₄·3 Cu(OH)₂·H₂O, Cu₂O
- 3) = 2° de manière analogue avec = 1°
- 4) = 4° de manière analogue avec = 1°, CuO
- 5) = 6° ZnO, CuSO₄·3 Cu(OH)₂, CuSO₄·3 Cu(OH)₂, CuO, Cu₂O
- 6) = 10° de manière analogue avec = 6°

ABSTRACT

Since 1986 the Nordiska museet in co-operation with the Swedish Corrosion institute has run a project on corrosion and corrosion protection of ethnological iron objects. Cleaning methods studied are blast-cleaning, rotating steel brush, electrolysis and EDTA. Methods of surface protection studied are waxes, oils, latex paint, lacquer, plastic coating, vapour phase inhibitor paper, drying agent and tannic acid. The results will be evaluated from both a technical and an ethical point of view. The climate and the rate of corrosion in a number of museums are recorded and a warning system for a corrosive atmosphere is developed. Some preliminary results are given.

KEYWORDS

Ethnology, iron, corrosion, museum, cleaning, surface treatment, appearance, climate

CORROSION ON AND PRESERVATION OF ETHNOLOGICAL IRON - REPORT FROM A SWEDISH PROJECT

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1. Introduction

In 1986 the Nordiska museet in co-operation with the Swedish Corrosion Institute started a four-year project concerning the protection of ethnological iron objects from rust. The project is financed by grants from The Bank of Sweden Tercentenary Foundation and has been accepted as a EURO CARE project.

In Sweden there are many museums with non-heated stores and exhibition areas, where temperature and relative humidity change very rapidly depending on outdoor weather conditions. Together with air-borne pollutants this causes an increased risk for corrosion and other damage. Even in museums with better facilities climatic and pollution factors sometimes give rise to corrosion. In the present project corrosion in ethnological objects of iron is studied with special reference to methods for cleaning and surface protection. The methods are evaluated from both an ethical and a technical point of view. Climate is recorded and wet time and corrosion rate are calculated at a number of museum sites in rural and urban areas.

The project is carried out by a team of conservators, curators and scientists. Members of the team are (1989) Jan-Erik Bergh, Ingrid Bergman, Maria Brunskog, Teje Colling, Bengt Nyström (chairman), Marie Louise Wulfrona-Dagel, the Nordiska museet and Mats Foghelin, Swedish Corrosion Institute. Björn Beverskog, Uppsala University, is a co-opted member of the group. The progress of the work is followed by a reference group with members from several museums.

2. Purpose

The entire study is aiming

1. to test under controlled conditions various methods for removal of corrosion products in combination with different protective methods. The protection methods are chosen among existing commercial ones and the testing is partly in collaboration with manufacturers.
2. to evaluate the corrosion rate during ordinary museum storage at several sites in Sweden.
3. to develop a simple "warning system" for corrosive environments.

The study has been limited to ethnological objects of iron. The reasons for this are the Nordiska museet's area of activity and the fact that fewer studies on corrosion on ethnological iron objects have been reported than on corrosion in the archaeological field.

The project is intended partly to provide advice for the conservation and storing of objects and partly to map environmental factors in museum buildings. It is obvious that the project will not result in one single recommended method. Rather, the conservator will be provided with a catalogue of advantages and limitations of the various methods.

3. Experimental work

3.1 Choice of methods

The choice of methods used in the project was based both on literature studies and on the experience of the members of the reference and research groups. After initial tests a number of methods were rejected and the methods described below remained. They represent dry and wet, mechanical and chemical cleaning, while the surface protective agents are waxes, oils, lacquers, inhibitors and drying agent. Both traditionally used methods and more modern ones are tested.

To enable an objective technical evaluation, cold rolled steel panels are being used for exposure experiments. The curatorial evaluation is based on old objects.

3.2 Steel panels

Cold-rolled steel panels, 100 x 50 mm, were exposed outdoors until they were completely covered with rust. Cleaning was then performed by the following methods:

- thorough blast-cleaning with glass beads (Sa 2 1/2 according to ISO** 8501-1)
- light blast-cleaning with glass beads (Sa 1)
- rotating steel-brush
- electrolysis in 1 M sodium hydroxide, with hydrogen formation, combined with mechanical cleaning with a soft brush (1)
- dipping in 0.02 M EDTA-disodium salt at 55 - 60° C, buffered to pH 8 and mechanical cleaning as above

The wet methods were followed by rinsing with demineralized water and drying with ethanol and warm air.

The cleaned panels were surface treated with

- a wax-type anti-rust agent designed for indoor storage, Dinitrol 81 ®
- a wax-type anti-rust agent designed for car protection, Dinitrol 4010 ®
- an oil-based anti-rust agent, Ferryl 103 ®
- a microcrystalline wax, melting point 73° C, acidity 0.0, Mobil Oil 2360 ®
- linseed oil with 1-2 % dryer
- acrylate latex lacquer without inhibitors
- cellulose lacquer
- a thick plastic coating, Crocell Super SH25 ®
- brushing with tannic acid (2).

Non-surface-treated samples were placed in heat-sealed polyethylene plastic bags containing

- a vapour phase inhibitor paper Artin Kores KR1300 ®, which was wrapped around the panel
- drying agent, silica gel, 40 g in each bag

In order to simulate non-heated storage conditions, the samples were exposed outdoors sheltered from precipitation and sunshine in the city of Gothenburg on the west coast of Sweden. (See fig. 1 and map fig. 3)

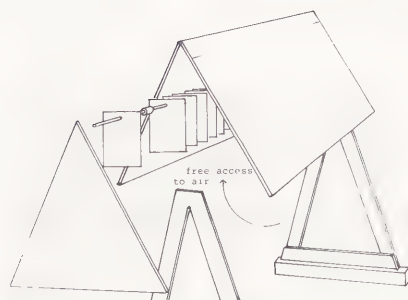


Fig. 1 Shelter for exposure of the steel panels. The panels are separated by small plastic tubes.

3.3 Engraved steel panels

As a complement to the above study we manufactured a number of steel panels with an engraved pattern. The object of this was two-fold; to see whether such a panel could also be used in the ethical judgement, as the ordinary panels are too anonymous and cannot serve this purpose and to use the engravings for various technical measurements. The measurements can provide information about the influence of the method on the object, remaining rust in the engravings and re-rusting patterns.

Some of the methods earlier used for cleaning and surface protection were considered unsuitable or unnecessary to test again. A second set of panels (engraved) were thus treated as follows:

- light blast cleaning with glass beads
- rotating steel brush
- electrolysis in sodium hydroxide
- dipping in EDTA-disodium salt

- Dinitrol 4010
- Ferryl 103
- microcrystalline wax
- linseed oil
- plastic coating
- silica gel

3.4 Antique objects

A number of old objects similar to those found in museum collections have been included in the investigation primarily to obtain a better basis for an ethical judgement. Some of these objects have also been exposed in the same way as the test panels. Fig. 2 shows one of the objects.



Fig. 2 A pair of candle-snuffers used in the ethical evaluation. (Photo M. Brunskog)

3.5 Ethical evaluation

In the planning of the project it was decided to evaluate the various methods in close co-operation between conservators/scientists and curators. The language and the approach of the scientist often differ from those of the humanist. Much time has therefore been spent on efforts to develop a model which could bring the two together.

Degree	Area rusted %
Ri 0	0
Ri 1	0.05
Ri 2	0.5
Ri 3	1
Ri 4	8
Ri 5	40/50

Table I. Degree of rusting (ISO** 4628/3) and rusted area in percent of the panels surface.



Fig. 3 A map of Sweden showing the sites for the exposure of metal coupons and steel panels.

1 Ajtte, Jokkmokk,
2 Sundsvall, 3 Svärdsjö,
4 Borlänge,
5 Skokloster Castle,
6 Stockholm/Skansen/-Svindervik,
7 Jultä,
8 Dingle,
9 Bovallsstrand,
10 Gothenburg,
11 Bungenuseet,
12 Hjärtenholm/Alvesta,
13 Marinmuseum/Karlskrona

3.6 Measurements of the corrosion rate in museums

In 15 museum buildings at 13 places in Sweden, most of them un-heated wooden buildings, the rate of corrosion of steel and copper is being measured (See map in fig. 3). Small steel and copper coupons fitted in a plastic holder have been placed at the different sites for evaluation after one year and after two and a half years. The evaluation is made by weighing of the steel coupons and by cathodic reduction of the copper coupons (3).

During the first year temperature and relative humidity have been recorded and the wet time calculated. The wet time is defined as the time when the temperature exceed 0°C and the relative humidity is 80 % or more. At four of the sites the levels of nitrogen dioxide, sulphur dioxide and soot have been measured during four weeks.

4. Results and discussion

4.1 Re-rusting of treated panels

The degree of re-rusting is expressed in the Ri scale (ISO** 4628/3), which is explained in table I.

Fig. 4 shows the degree of rust on panels without engraving after 21 months of exposure. Fig. 5 gives the values for engraved panels exposed for 12 months.

The cleaning methods which have shown the least re-rusting are electrolysis, brushing with tannic acid and hard blast cleaning (See figs. 4,5). The cleaning methods must, however, be evaluated in combination with the surface protection. Obviously the combination of hard blasting and storing the panel in a heat-sealed polyethylene plastic bag containing silica gel gives complete protection providing that the silica gel is changed often enough, in this case every six months. Other methods have also given good results: linseed oil, microcrystalline wax, Dinitrol 4010, Ferryl 103 and plastic coating. Even though there was little corrosion on the surface of the panels treated with linseed oil, there were blisters in many cases and damage on the edges on almost all panels. Microcrystalline wax gave a good protection to carefully cleaned surfaces but was relatively easily mechanically damaged and gave in many cases insufficient protection for the edges. The edges posed a problem also with Dinitrol 4010 and Ferryl 103, which are both sensitive to mechanical damage.

The other methods did not give satisfactory results. Brushing with a rotating steel brush did not remove all the corrosion products. It was, however, the only method which gave the surface a metallic lustre. The panels cleaned with EDTA re-rusted very rapidly before the surface treatment. Brushing with tannic acid gave the panels a brownish colour and it caused blistering on the surface protection applied (linseed oil or microcrystalline wax). Light blast cleaned surfaces were more easily re-rusted than those subjected to hard blast cleaning. Acrylic water-borne lacquer without corrosion inhibitors gave a most unsatisfactory result. The method was included because of the wish to use a product without solvents which can cause health hazards. Panels treated with cellulose lacquer (Zaponlack) also showed much corrosion after exposure. The reason for including this method was that it has frequently been used in conservation and has a reputation as a "good old method".

4.2 Ethical evaluation

The methods for ethical evaluation are still under discussion and the results will be presented later. It is, however, evident that the hard blast cleaning will not be accepted.

4.3 Steel and copper coupons

The corrosion of steel, expressed in weight increase (g/m^2), and of copper expressed in the thickness of the layer in Å is shown in figs. 6,7. The wet time for the different sites is presented in Table II together with a brief description of the type of building.

According to a classification in a recent Czechoslovakian investigation (4) all the museums except Hjärtenholm (see map fig.3) can be characterized as having a climate with a low corrosion risk and even at this museum the corrosion rate would be acceptable. This characterization has not, however, been constructed for museum objects. As a deterioration caused by corrosion which is small expressed as weight gain, may still have a very serious effect on the surface appearance, the need for a classification adjusted to the museum should be considered. Efforts are being made to construct such a scale.

5. Conclusions

The investigation has so far permitted some preliminary conclusions to be drawn.

5.1 Suitable cleaning methods

Light blast cleaning can be used in some cases. However, it changes the appearance of the surface and does not remove all the rust, which can cause re-rusting.

Electrolysis gives a cleaned but darkened surface.

Tannin can be accepted for the treatment of outdoor objects.

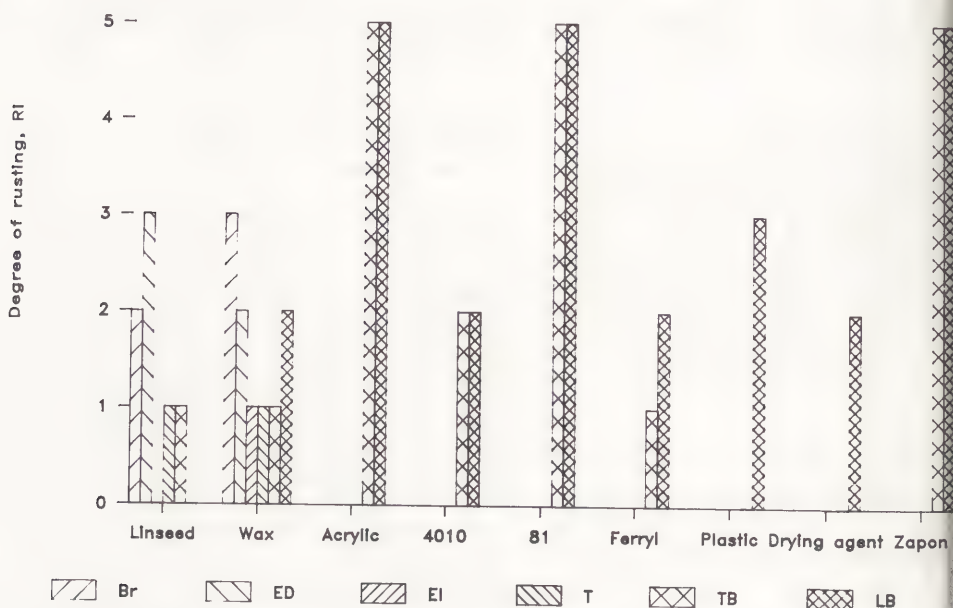


Fig. 4 Degree of rust (according to ISO** 4628/3) on cleaned and surface-treated engraved panels after 21 months exposure under cover in Gothenburg. The surface protection methods are from the left: linseed oil, microcrystalline wax, acrylic latex laquer, Dinitrol 4010®, Dinitrol 81®, Ferryl 103®, plastic coating, drying agent, cellulose laquer. Br = rotating steel brush, ED = EDTA disodium salt 0.02 M solution, EI = electrolysis in sodium hydroxide, T = tannic acid, TB = thorough blast-cleaning with glass beads, LB = light blast cleaning with glass beads.

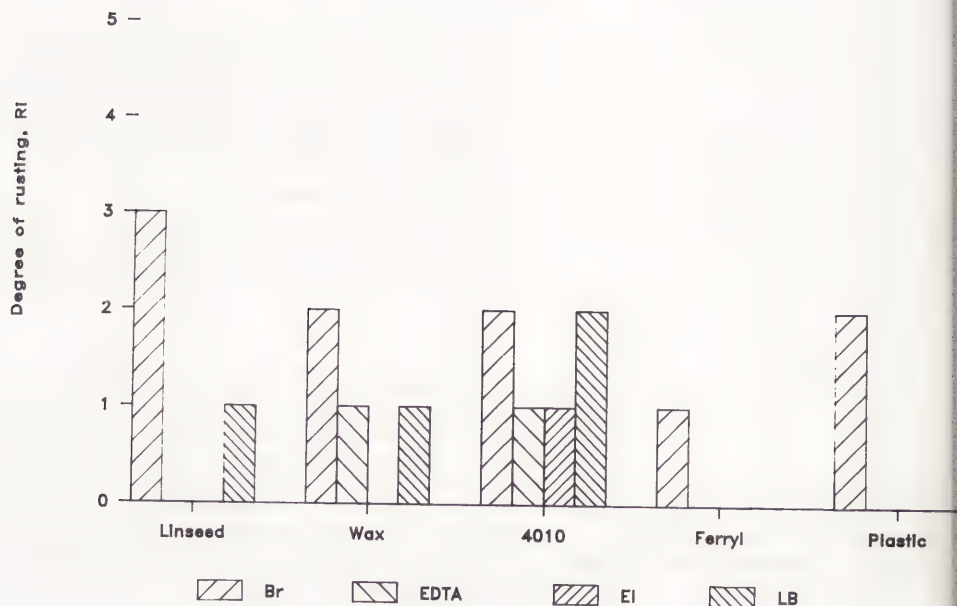


Fig. 5 Degree of rust (according to ISO** 4628/3) on cleaned and surface-treated engraved panels after 12 months exposure under cover in Gothenburg. The surface protection methods are from the left: linseed oil, microcrystalline wax, Dinitrol 4010®, Ferryl 103®, plastic coating. Br = rotating steel brush, EDTA = EDTA disodium salt 0.02 M solution, EI = electrolysis in sodium hydroxide, LB = light blast cleaning with glass beads.

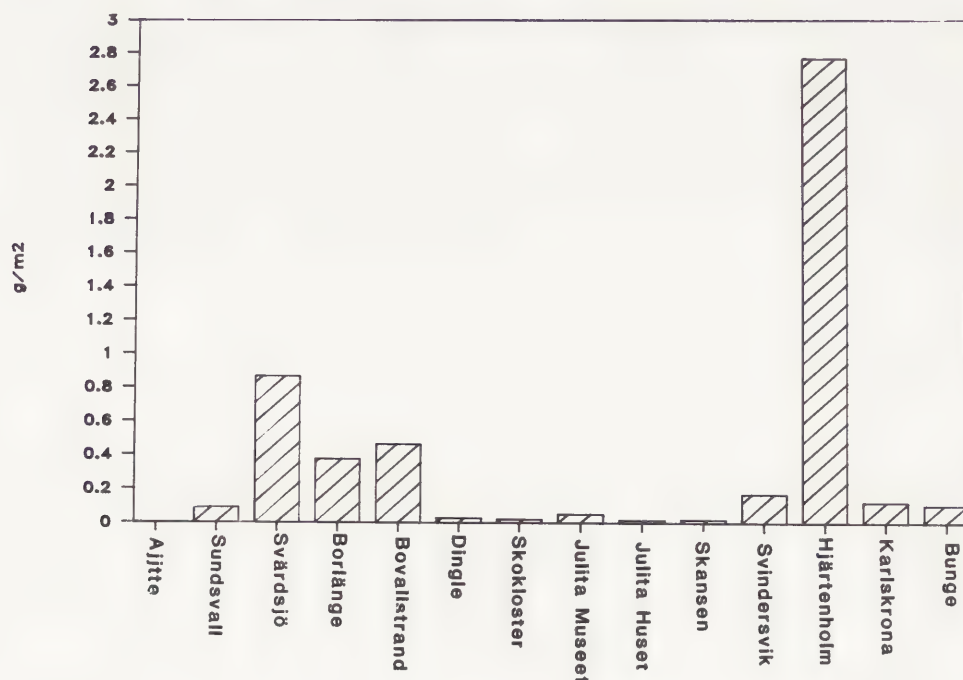


Fig. 6 Weight increase on steel coupons which have been exposed in museums for one year. See also map in fig. 3.

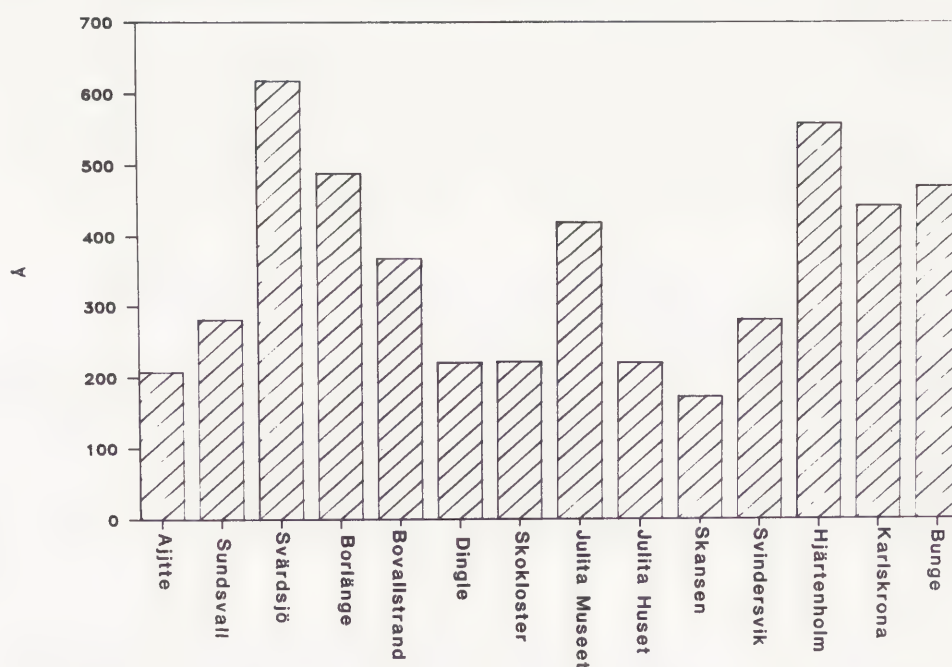


Fig. 7 The thickness of the layer of corrosion products on copper coupons which have been exposed in museums for one year. See also map in fig. 3.

5.2 Suitable surface protection methods

Dinitrol 4010 has proven to give a good protection during one year's exposure, but it must be re-applied periodically depending on the storage conditions and climate.

Ferryl 103 gives good protection, but the surface is brown coloured and the drying time is extremely long.

Microcrystalline wax gives a good corrosion protection but is easily mechanically damaged.

Linseed oil also protects well against rust but it needs careful surface cleaning to avoid blistering.

Plastic coating can be used in special cases.

MUSEUM	CONSTRUCTION	WET TIME (HOURS)
Ajtta 1 #)	Modern climatized museum	0
Ajtta 2	Wood panelling, tin roof	486
Sundsvall	Wood panelling, tin roof	1067
Svärdsjö	Log walls, tiled roof	2896
Borlänge	Log walls, tiled roof	852
Skokloster Castle	Plastered brick framework	2313
Skansen/ Skogsholm	Plastered log walls	2445
Svindersvik	Partly rough brick walls, partly wood panelling	2886
Julita/Museet	Log walls	2232
Julita/ Stora Huset	Plastered brick walls	1699
Dingle	Panelled log walls, tiled roof	2501
Bovallstrand	Panelled log walls, tiled roof	2539
Bunge/ Lunderhagestugan	Wooden walls and roof	4892
Hjärtenholm	Combined stone and wood construction, eternit roof	1906
Marinmuseum/ Inventarie-kammare 2	Wooden balk framework, wooden panel, felt roof	1985

#) Ajtta 1 will be evaluated in 1990

Table II. Construction of the buildings where metal coupons have been exposed. In the right column is given the wet time in hours for the first year of exposure.

Vapour phase inhibitor paper and silica gel both give a very good corrosion protection but need to be renewed periodically.

5.3 Measurement of the corrosion rate in museums

The corrosion rate in museums can be evaluated by small steel coupons which are weighed very precisely before and after exposure. An indication of the results can be obtained by visual inspection. The method can be used as a warning system for a corrosive atmosphere. The corrosion rate in similar museum buildings seems to depend more on the microclimate in the building than on the geographical location.

6. References

1. H.J. Plenderleith, A.E.A. Werner, The conservation of antiquities and works of art (London:Oxford University Press, 1977), 285-86.
2. J.B. Pelikan, "Conservation of Iron with Tannin," Studies in Conservation 11, no.3(1966): 109-114.
3. W.E. Campbell, U.B. Thomas, "Tarnish studies. Electrolytic reduction method for the analysis of films on metal surfaces," Electrochem. Soc. 76 (1939): 303
4. L. Cervený, "Diagnoza a prognoza korozního namáhání kovových výrobků při skladování v krytých skladech," Strojirentsvi 38, no.4 (1988): 245.

7. Materials

Trade name	Composition	Manufacturer
Dinitrol 81 ®	saponified ester-waxes white spirit	Dinol Int. AB Box 149 S-281 22 Hässleholm Sweden +46 451 80000
Dinitrol 4010 ®	polyester-modified wax dispersion neutralized fatty acids waxes, inhibitors aliphatic petroleum solvent	See above
Ferryll 103 ®	petroleum based oils and fats inhibitors stabilizers	AB Ferryll Box 120 S-245 00 Staffanstorps Sweden +46 46 255050
Mobil Oil 2360 ®	white spirit microcrystalline wax	Mobil Oil Corp. 3225 Gallows Rd Fairfax Virginia 22037-0001 U.S.A. +1 2203370001
Crocell Super SH ®	cellulose ester vegetable oil phthalate ester antioxidant	Croda Application Chem. Churchill Road Doncaster South Yorkshire England DN1 2TH +44 0302 27451
Artin Kores KR 1300 ®	amine nitrates	Artin-Kores AB Hanholmsv. 51 S-602 22 Norrköping Sweden +46 11 180230

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** ISO = International Standard Organisation

ABSTRACT

The "Golden Gun" is a rare example of the prestigious artillery of the 17th century. The restoration of the gun barrel became necessary in view of the condition of the object and the loss of the handle and the breech head of the central muzzle. Since only scarce details were known about the structure of the gun tube, complicated technological investigations had to be undertaken. At the same time investigation methods had to be applied which could be carried out by uncomplicated means at the restoration workshop. The composition of the patina in the bore and chamber and a possibility for its preservation, of the reconstruction of the handles and the breech head of the central muzzle and their fastening to the original, are described.

KEYWORDS

Examination, detail completion, restoration of a gun barrel

INVESTIGATION AND RESTORATION OF THE GUN BARREL OF THE "GOLDEN GUN" OF THE 17th CENTURY

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Introduction

The "Golden Gun" - inv. no. 481 - of the Museum of German History in Berlin belongs to the rare preserved examples of specific artillery structures of the 17th century (fig. 1). The gun owes its name to its fire gilded surface. With a length of 2965 mm and a diameter of 224 mm at the base molding, it corresponds to the proportions of a falconet. The tube lies in a shell carriage of oakwood with a 6 mm pear wood veneer. All the ironwork is richly embellished with engravings. The engravings include the letters H.R.M. and the year 1643. These indications did not suffice hitherto to identify the producer or his client. The first reference to two "Golden Guns" in Hamburg was made in a text dating from 1675. One of the two entirely similar guns remained in Hamburg, whereas the other was moved to Berlin in 1896. Another gun made by H.R.M. in 1640 is in the Military Museum in Vienna. All three guns are distinct for their gilding, abundant ornaments and presumably similar construction principles as prestigious models.

The condition of the "Golden Gun", the damage caused during the Second World War and losses of details, called for restoration. Since little was known about the structure of the gun, preliminary investigations exceeded the scope of requirements for restoration.

Investigations of the structure of the gun tube

The tube is not made of one piece, like bronze gun barrels, but of thin metal and light organic material layers. This accounts for the light weight of only 150 kilogrammes. The first insights into the layer structure were obtained after the dismantling of the trunnion. The copper coating was interrupted on a width of 62 mm, baring the layer of leather underneath, which was fixed to a layer of pinewood. Other details were identified by means of radiography. This is an investigation method applied to industrial materials testing, which causes no damage and has frequently proved successful in museum work. The gun tube was exposed to hard gamma radiation emitted from a portable radioactive radiation source, Indium -192. Photographic films size 100 x 200 mm served as radiation receivers. A total of 10 exposures were made of various parts of the gun tube with an exposure time between

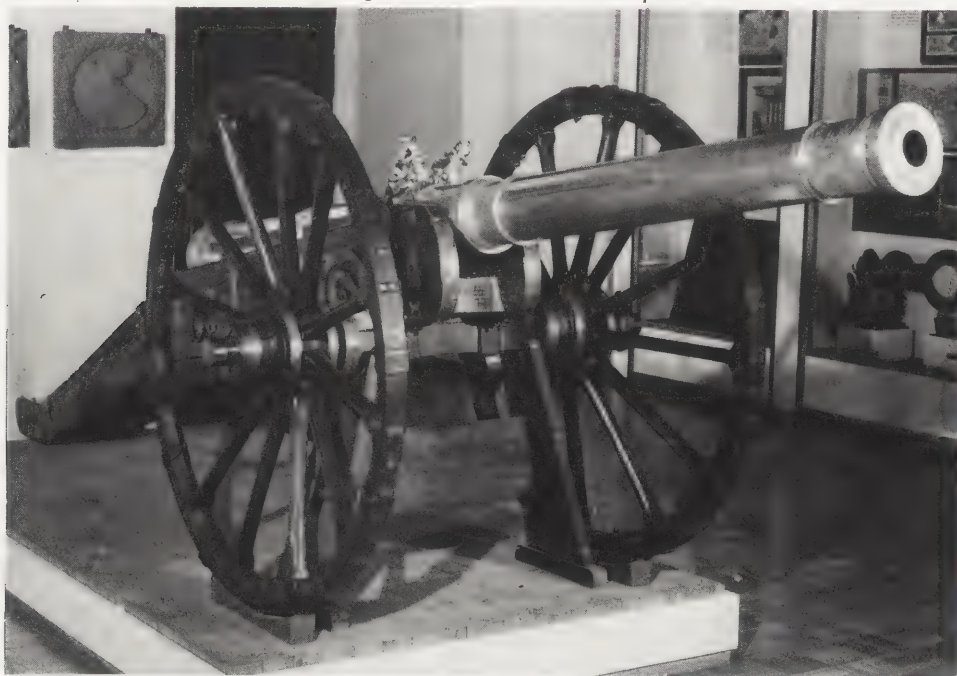
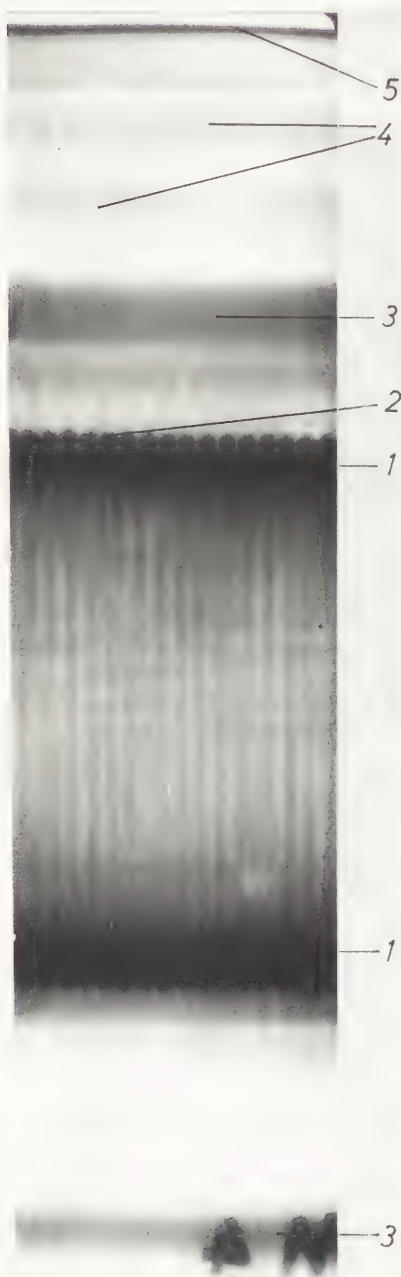


Figure 1



3 and 10 minutes. Interpretation of the photos was quite complicated at first, since no comparable information was available. Figure 2 shows the positive of a photo of the tube cross section. There are the distinct outlines of a copper bore tube (1). Above it there is an iron wire coiling (2). The wire has a diameter of 3.5 mm. The density (3) is caused by iron bars in a parallel position to the bore axis. Other layers of organic material (4) and the outer copper shell (5) can be recognised.

Other knowledge was obtained with the aid of an endoscope. In an already existing small bore, which penetrates the layers up to the wire coiling, the layer sequence could clearly be ascertained. Thus there are two layers of pine wood under the leather layer, and two hemp rope coilings.

The iron bars marked on the radiographic photos could be simply ascertained with the aid of a beam balance (fig. 3). One balance pan of the beam balance was replaced by a permanent magnet and tared so that the permanent magnet was suspended above the tube. If an iron bulk came into the magnetic field of the permanent magnet during turning of the tube, this was indicated by the balance. In this way the position and length of four iron bars could be ascertained. The sum of the different results of investigations gave an image of the structure of the tube (fig. 4). A copper bore tube (1) is covered by coiled wire (2). This is followed by a hemp rope coil (3), above it a pine wood layer (4), another hemp rope coiling (5) and the last pine wood layer (6) with the inset iron bars (7). The leather layer (8) is the uppermost layer of organic material, enveloped by the outer fire gilded copper casing (9).

This revelation proved that the fundamental structure of the gun was very close to that of the Swedish leather guns; these had been used by the Swedish army as light field artillery between 1627 and 1632.

Bore and Chamber

The condition and the corrosion products of the inner surfaces of bore and chamber were of particular interest. The bore has a length of 2560 mm and a caliber of 68 mm, with a joined 204 mm detached powder chamber of 57 mm in diameter. The vent of the central detonator begins at the breech face and ends in the chamber. These interior surfaces had to be visually investigated over a length of 2764 mm and photographed for the documentation. Furthermore it was necessary to extract particles of the patina from selected places for analytical investigations.

A simple optical mechanical device was produced in order to comply with these requirements. The basic idea was the introduction of a plane mirror and a light source into the tube and to take photos from the outside with a long-focus lens and to conduct visual observations with an eye piece. Samples of the patina were to be taken by means of a controllable procedure with the

Figure 2

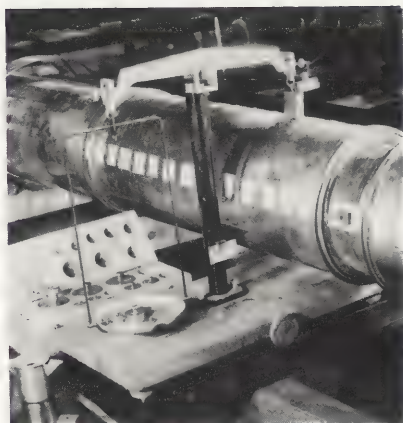


Figure 3

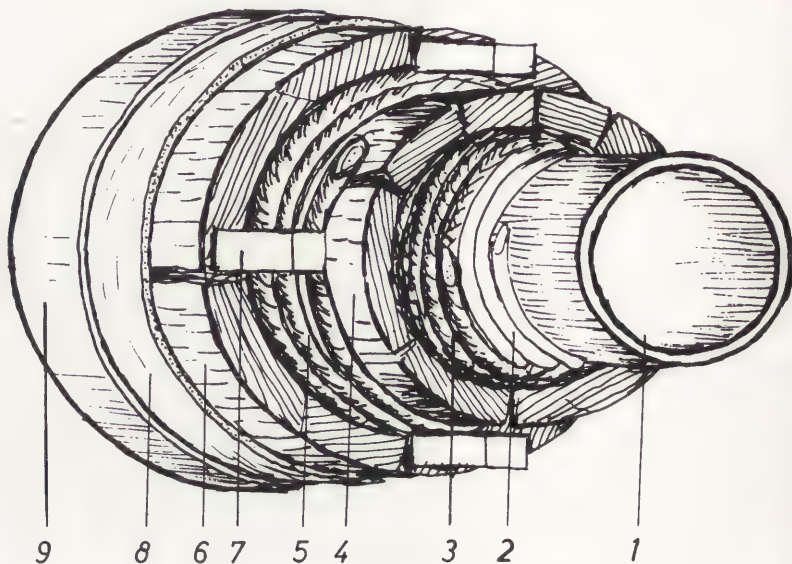


Figure 4

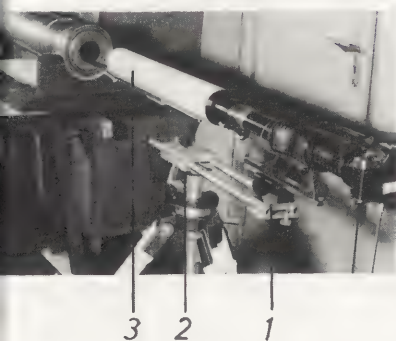


Figure 6

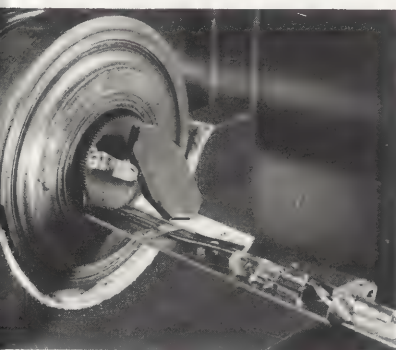


Figure 7

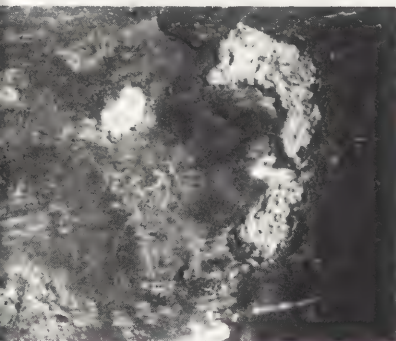


Figure 8



Figure 9



Figure 10

aid of a steel blade. Figure 5 shows the instrument developed. A sliding carriage (1) holds a rotary mirror with a silver-plated surface (2). This is inclined at an angle of 45° to the optical axis and thus also to the axis of the bore, fastened to a vertically standing cogwheel (3) so that it can be turned from the exterior by way of a smaller cogwheel (9) and a shaft (4) over the connection piece (10). The mirror shows a part of the bore and the chamber 40 mm wide, which is visible by the rotation of the mirror over a range of 300° . A halogen lamp of 12 V; 100 W (5) is used as illumination. It is operated with low tension voltage in visual observation, in order to reduce heat development and thereby air disturbance within confined space. For photography the lamp is operated at full tension. It was found that this increased the air turbulence to such an extent that the finest dust particles stirred up caused the formation of a veil. A solution of this problem was found in sucking off the air through the vent. The extraction of corrosion products was operated by means of a movable arm (6) to which a steel blade is attached (7). This arm is lifted by a taut wire, the blade is pressed against the interior surface and the corrosion particles are lifted off. The loosened particles are caught by the glass container (8). Mirror and camera are firmly linked by levers. The distance of the object and the scale of recording are unchanged over the entire length of the barrel. Lens and camera are outside the tube (fig. 6). They are linked by a support bridge (1) and mounted on a stable studio tripod. A telescope (3) with an achromatic lens of 63 mm aperture and a focal length of 840 mm served for visual observation and as camera lens. The casing of a Praktica MTL 5 is used as camera. Figure 7 shows the mirror in front of the muzzle opening.

The visual observation showed that the entire interior surface was covered with a dark brown patina, broken in many places and filled with green corrosion products (fig. 8), or covering the surface (fig. 9).

A longitudinal seam was clearly visible (fig. 10) which allows the conclusion that the tube consisted of a rolled tin plate. A total of 480 mg substance was taken as samples of ten characteristic corrosion symptoms. A microchemical analysis ascertained carbonates and sulphates. The X-ray fine structure analysis finally allowed a reliable assessment of the patina. The main components ascertained were: malachite, tenorite, arcanite and brochantite. The formation of tenorite, malachite and brochantite can be explained by the known corrosion processes in copper. The arcanite (potassium sulphate) is a component which cannot be included in the corrosion processes. The presence of potassium sulphate is very probably due to the combustion of black powder. In that process 56 per cent of the powder substance remains as firm component with 8.5 per cent potassium sulphate.

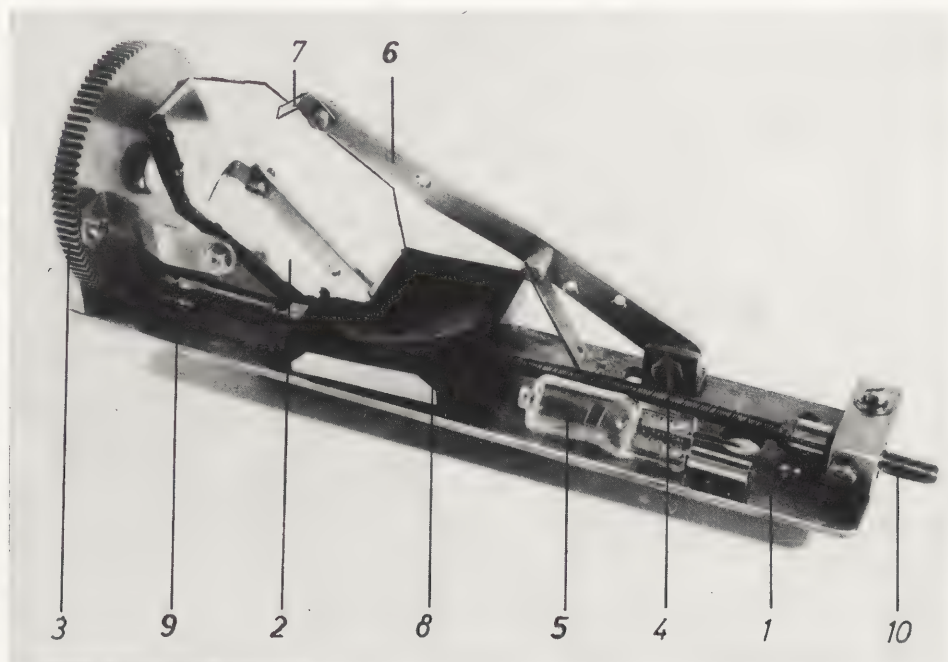


Figure 5

The conclusion might be drawn that the gun was fired, but since the surfaces of the bore showed no traces such as are left behind in bronze guns by solid projectiles, it may be assumed that only ballards had been fired. These observations consolidate the assumption that the gun was a show piece not serving purposes of war.

The decision had to be taken whether to remove the patina and to conserve the exposed metal surface, or to preserve it. Preference was given to the preservation of the patina, since this was a rare case of patina so little affected by weather conditions within more than 300 years. Nor were there any aesthetic or material technological reasons for removing it. The vent and the bore were closed at a distance of 200 mm from the muzzle, in order to protect the patina against transformations.

The air remaining in the bore and chamber was dried to a relative humidity of 8 per cent by silicic gel, creating a microclimate largely preventing electrochemical corrosion processes. A hard foam polyurethane plug (fig. 11, B) was inserted into the vent. Figure 11 A shows the breechblock mechanism part of the bore. Two acrylic disks (1) are drawn together by the screw (2); this causes the polyurethane ring in between (3) to arch and press against the tube wall. The gauze container (4) holds 100 g silicic gel. This may be observed in the inserted condition of the breechblock through the acrylic disks.

Reconstructions

The principal ornaments of the "Golden Gun" included the handles in the shape of wrestling Tritons and the elephant's head - the breechblock mechanism of the principal ignition. These parts have been lost and had to be replaced by reconstruction. It could be presumed that these ornamental parts of the gun existing in Hamburg were more or less identical with the lost parts of the Berlin model. It was therefore legitimate to use the forms of these parts of the gun in Hamburg for the reconstruction.

The silicone rubber forms allow replica in the most varied techniques. Attempts to produce galvanoplastic copies and synthetic material casts yielded unsatisfactory results. Good results were only obtained with the bronze cast.

Wax casts were produced in the molds, which served as models, after retouching, for the lost shapes in the way melting procedure. The cast was made in bronze and thereby the material and production technology corresponded to the originals. The reconstructions are smaller than the original due to the addition of the shrinkage measure in the different manufacturing stages.

Figure 12 shows the handles fitted onto the tube, and figure 13 the screwed on elephant's head. The recognition of the parts as reconstructions was facilitated by marking with the figure 89.

Frequently screws or parts of museum exhibits need to be supplemented by threads or coils. These have thread pitches, angles, diameters and profiles considerably divergent from those of modern threads. Each thread therefore has to be individually made and adjusted to its counterpart. Two variants of thread

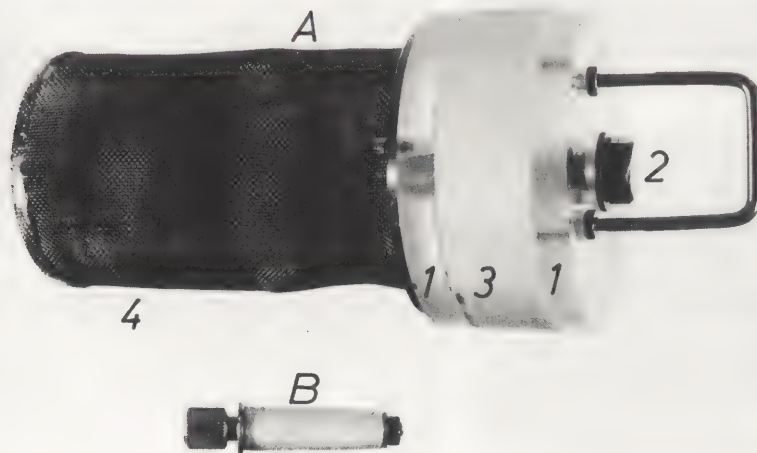


Figure 11



Figure 12

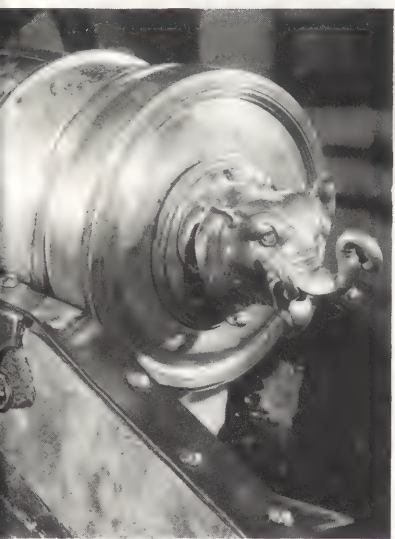


Figure 13

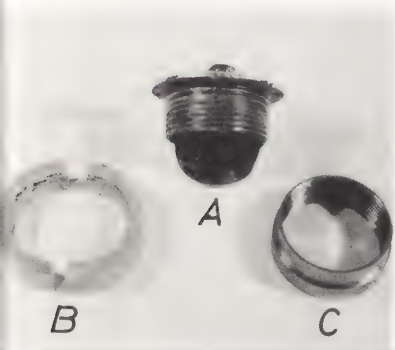


Figure 14

manufacture were tested in the mounting of the elephant's head. In the cast part of the head a threaded ring had to be fastened in such a way as to allow the head to be screwed on to the thread connection (fig. 14, A) on the breech face on the gun. The thread connection has a diameter of 57 mm, a thread pitch of 2.8 mm and a screw thread angle of 101° .

First Variant

A wax layer was applied to the original threads of the connection as separating agent and the thread was poured off with plastic substance. A two-part tap was made (fig. 14, B), which could be stuck into the elephant's head.

Second Variant

The thread is made on an engine lathe. The thread was cut into a metal ring (fig. 14, C) with a shaping tool. This required the translation of the pitch of the engine lathe from 3 mm to the pitch of the tap of 2.8 mm, with the aid of interchangeable gear with different tothing numbers. The problem always consists in whether interchangeable gear with the required tothing numbers is available. In the present case only an approximate value of 2.84 mm was achieved with the interchangeable gear. In view of the large tolerance and the shortness of the old thread the pitch error of 0.04 mm in each course of thread could be neglected. This variant of the metal ring proved to be the better solution, despite the lesser degree of precision of the thread.

Conclusion

The principal task in the restoration of the "Golden Gun" consisted in the investigation of manufacturing techniques, substantiated by analytical methods, the analysis of corrosion products and their treatment, and the replacement of missing parts. The surface treatment of the object was a marginal problem. It was confined to uncomplicated, conventional methods, by the application of protective covering and partial retouching with gold colour pigments.

ABSTRACT

Presented is a chronological review of the history of the application of XRF to archaeological research. The effective application of XRF will be described, as well as the many difficulties and sources of error of the method. It is also suggested that perhaps some "old-fashioned" semi-quantitative methods employed by our grandfathers (e.g., electrography) could return to the lab again, in cases where such simple methods would be quite adequate. An extensive bibliography is included.

KEY WORDS

Archaeology, alloys, analyses, methodology, x-ray fluorescence spectrometry (XRF).

ANALYSES OF ANCIENT ALLOYS: RETROSPECTIVE CONSIDERATIONS

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INTRODUCTION

Scarcely more than fifty years ago, physics started its tremendous progress in the field of nuclear methods, microelectronics, etc. These developments, in turn, found immediate practical applications, from spacecraft technology to common problems in kitchens and laboratories; they also found their way into the fields of conservation and archaeology.

The need for the chemical analysis of objects (particularly metals) was well recognized. But wet chemical analyses were more or less destructive, and often involved cumbersome analytical operations. The new physical methods for chemical analyses were welcomed, as they were clean, quick, and nondestructive. The readings were automatically registered and could be repeated as many times as necessary. Archaeologists were fascinated with this new tool of microphysics, which enabled them to enter so deeply into the mysteries of ancient materials. Thus was archaeometry born.

X-ray fluorescence spectrometry (XRF) was found to be far more helpful than other physical techniques for chemical analyses, and will be the main point of consideration in this report. Although XRF provides much excellent data, its limitations as a technique must be understood.

X-Ray Fluorescence Analysis (1953-69)

The general possibility of using XRF for chemical analyses was already recognized when Hall noted in 1953 that the method could find application in "...the analysis of pigments used in pictures and other works of art." Some years later Hall again mentions the method, this time in the context of archaeology, as "perhaps the most powerful weapon in the nondestructive (analytical) armoury" (1958). He also mentions the installation of an apparatus for XRF analysis in the New Research Laboratory for Archaeology and the History of Art in Oxford. The use of this technique was considered a step toward further development and cooperation between scientists and nonscientific archaeologists.

Hall's research (1960) applies XRF analysis once again to archaeology and mentions the technique as a "now well established method of analysis both in the laboratory and industry. The fact that the method is essentially non-destructive makes it particularly attractive for the analysis of a archaeological and museum artifacts." But after a brief description of basic scientific principles, Hall warns the reader that in the case of surface contamination or enrichment, or a lack of homogeneity in the sample, the analytical result "may be very difficult to interpret." This particularly concerns metal objects, including ancient coins. Hall (1961) offers more cautionary advice in a discussion of the possible causes of surface enrichment.

Next comes the problem of proper sampling. Jedrzejewska (1962) considers this problem generally, stating that the determination of original metal composition is equally unreliable for objects covered with a layer of corrosion products, and those previously cleaned. Organ (1962) is an optimist and believes that the original composition of the metal stays unchanged under the thin surface layer of corrosion. This subject is of great importance because the "miraculous" X-rays have a very low penetration power and give analytical information only about the surface region to a limited depth; this region must be representative of the whole to make the analysis reliable. The issue of proper sampling is again raised by Hall and Roberts (1962), and discussed in terms of a particular specimen. The problem of sampling is also known in industry. Dozinél (1963) states that "good sampling can be more important than a good analysis." So not only is the physical side of the method of basic importance, but also aspects of the analyzed object itself. Hall (1963) states that conclusions drawn from XRF data may be misleading, if the results are overinterpreted. This is particularly important for coins and other small objects always susceptible to surface corrosion.

Young (1963) studied the inter-element effects inside the sample matrix, which may either absorb or enhance the emitted secondary

radiation. There is need for corrections in calibration curves and in the standards of reference, as these parameters may affect the final reliability of the readings. To eliminate possible errors, a recipe is given for the preparation of standard specimens by compressing chemically pure metal powders.

Limitations due to the presence of misleading surface deposits certainly reduce the number of objects suitable for XRF analysis. Carter (1964) recommends the cleaning of coins "for accurate XRF analysis" by air-blasting with aluminum oxide powder; detailed considerations on surface depletion are included.

Another limiting factor is the internal heterogeneity of a sampled metal. Condamin and Picon (1965) consider in detail the possible diffusion phenomena in ancient alloys, and Hall (1961) points out some mechanisms that may be responsible for surface enrichment. The awareness of the number of factors limiting the operative range of XRF was evidently growing, signalling the need for methodological reflections. In 1964, Caley presented a timely critical evaluation of published analytical data, including that on metals. He opens his paper with these comments: "The thousands of quantitative analyses of ancient materials that have been published differ widely in their accuracy, reliability, and usefulness. A considerable proportion, certainly over half, are defective in one or more ways. . . In the first place much carelessness and vagueness about sampling procedure is apparent in many reports of analyses. . . it is usually uncertain whether the analytical data represent the composition of a local area, a larger spot of the object, or the whole object, in present, or the original unaltered condition." Besides problems of sampling and cleaning, the manner in which results are presented, the accuracy of the description of objects, etc., may also be questionable. All this may make the final conclusions questionable as well. There are many other valuable comments. Caley ends his paper stating that "It is the hope of the author that his paper will serve as a useful guide in the preparation of better reports in the future."

XRF and other physical methods of analysis (1970-1988)

The analytical limitations of XRF were well recognized in 1970, and careful attention was usually paid to well-controlled experimental conditions. But XRF was also considered by many investigators to be an already "routine" operation, and more attention was being paid to the results than to the research method. However, some experimentation and research was done to make the readings more reliable and to understand better the internal structure of ancient alloys.

Metcalf and Schweizer (1971) consider in some detail the problem of the selection of calibration standards, which relate to the actual concentration of elements in the alloy's matrix. Brown and Schweizer (1973) describe a method of analysis used to examine a sample of Anglo-Saxon jewelry. First a qualitative scan was done to assess the elemental composition of the alloy. Then a suitable spot (1-2 mm²) was selected. Readings were taken step-wise: first on the uncleaned surface; then after mechanical cleaning with a fine surgical scalpel; the testing and cleaning was repeated until no more change in the readings were observed. The results were compared with data from wet chemical analysis. Charles (1973) studied variations in micro- and macrostructural heterogeneity in alloys that could influence the analytical readings. They may be a result of solidification from metals, and also alterations due to high-temperature working, reheating, and eventual subsequent corrosion.

Jedrzejewska (1981) commented on XRF from the methodological point of view. XRF data requires a "translation" of indirect physical instrumental readings into a meaningful chemical description. Hence, comparative standards are necessary for calibration curves. The "samples" or analyzed fragments, have to be representative of the object as a whole. Interelement effects of X-ray absorption in the matrix elements have to be taken into consideration, as well as the possible heterogeneity of the object and sample. A critical evaluation of all these factors should accompany every report, with a comment on possible factors of uncertainty.

But notwithstanding all the limiting factors, the XRF method is still a very useful tool in the analytical examination of ancient alloys. The instrumentation is relatively simple and the apparatus is portable. And it can be applied to any size object.

Other nuclear activation methods

While XRF was being developed as a research method, other nuclear activation techniques were being introduced into the field of art and archaeology. A historical review of published materials is given by Sayre and Meyers (1971), as an Appendix in AATA. There were four main methods applicable: (thermal) neutron activation, fast neutron activation, charged particle activation, and high energy photon activation; XRF belongs to the last group. For metals, thermal neutron activation is often applied to small precious objects (e.g. coins), because it gives information on the composition of the whole, not only of the surface, in a properly quantitative manner.

Neutron activation analysis (NAA) was first reported in 1953; as a technique it is contemporary to the XRF. Aitken (1961) describes the method in his book, with references to earlier works by Emeleus (1958) and others. Generally, the method is considered to be one of the most powerful tools for the analysis of metal objects. This method is widely applied, as can be deduced from the reports in recent volumes of AATA. A good summary of the present state of instrumentation and techniques of analysis was given in excellent reports by Baer and Low (1982) and by Mairinger and Schreiner (1982). There is a comment in the paper by Baer: "Of critical importance to the analysis is the selection and preparation of the sample. The smaller the sample the greater the possibility that it is non-representative. To minimize this source of error, it is essential that the conservator/curator participate in sample selection and have full understanding of the limits of the analysis. The foregoing implies that the oft-mentioned concept of central laboratories providing nation-wide analytical services may require re-examination." Also discussed is the growing cost of these very complex analyses and their place in routine conservation practice.

Simple methods

A method is like a tool. Before using it we should ask whether this tool (which may be excellent in itself) is really the one we need for the intended purpose. Perhaps we are not experts, or our budget is inadequate, or the tool has limited application or is too sophisticated for our need. These considerations easily apply to the analytical examination of ancient metals, with all the above mentioned methodological elements duly respected. Here, it is interesting to cite the opinion of Cope (1973). "It is unfortunate that nondestructive methods of chemical analysis almost always involve variable factors of uncertainty. This is partly due to indirect measurements having to be made by means of physical phenomena which may not be chemically specific and free from matrix or other interferences effects, and partly because of the unknown extent of internal heterogeneity and corrosion upon either the complete object or the fractional sample taken. (The effects of segregation or corrosion are, however, unlikely to be properly discerned without recourse to some form of destructive examination). In consequence, the concept of a destructive metallurgical examination, and chemical analysis by absolute methods is often abandoned prematurely with insufficient regard to their full potentialities of reliability, accuracy and completeness."

Between the time of the development of completely destructive analyses and the nondestructive physical methods there was an interval of transition. A combination of chemical and physical processes was used, mostly based on chromatography or colorimetry, on the semi-micro scale, sufficient for research needs but cumbersome in detail. Although these methods seem very old-fashioned, they do not need complicated instrumental equipment and may be carried out in almost any laboratory with one qualified specialist. In many cases these techniques give all the information that is actually needed, and answer many conservation questions. Perhaps these methods deserve new consideration, even if they seem naïve and démodé.

This author has investigated the efficacy of "simple methods" and accompanying "spot tests" since the 1967 ICOM Questionnaire, and has prepared a general outline of semi-quantitative determinations by confined-area techniques (Jedrzejewska 1972). Two such techniques are the Schelicher and Schüll "Yagoda confined-area spot-test papers" (100mm²) and this author's "Confetti" 7mmØ). Sampling was to be done by the very popular "electrographic" method. A review article by Wawrzyczek (1959) gives a detailed description of its history and development.

Electrography is a semi-quantitative and semi-micro analytical technique. Sampling is done by electrolysis, and detection of elements by spot tests. It was invented by Glazunov in 1929, and quickly found wide application in metal industries, geology, etc. During the war, a "Portable Electrographic Kit" for the easy field determination of 18 elements was produced in Philadelphia. Several types of electrodes and arrangements were designed for different purposes, and various specific reagents were tried by Jirkovsky, Hál, Stembrok, and others. The method was very popular in many countries, and particularly in the USA. A separate Section of Electrography was created in 1948, in Washington, at the Congress of the American Chemical Society. Also a book was published on this subject by Hermann and Wadlow (1951). Then the method somewhat disappeared from sight.

Recently, Laver (1978) gave renewed attention to this procedure and compared it, with good results, to other spot-testing systems. A recommended list of reagents was given, in addition to comments and a diagram of a rather primitive testing arrangement.

The name "electrography" was lost but the method certainly can find a good analytical use. Electrography may be well applied to ethnographic objects (Pearson, 1988); Jánoska (1987) also mentions it in his report on the conservation of a Roman harness. With regard to small but unusual contributions to research in simple methods, the work of Mahon and Benedetti-Pichler (1960) is of interest. They describe the easy, qualitative or even semi-quantitative chromatographic separation of ions on a hanging thread serving as substrate. One drop of test solution only is required.

Perhaps it might be good to start hunting for some more of these forgotten, "simple" analytical procedures.

Comments

This retrospective review clearly demonstrates the wide range of existing analytical procedures for the analysis of ancient metals. In fact, there are no ideal methods, objects, or analysts; the ideal lies in good compromises.

There also is an obvious quality of interests and situations between scientists and archaeologists in ways of thinking, and in the professional "hermetic" language. Quality exists also in the objects: between surface and total (bulk) measurements, between the original and the actual composition. In measurements, this same quality is seen between the real needs and the optimistic desires; in the choice of methods, there is often a disparity between the needed information and the available funds.

It also seems that there is an obvious lack of uniformity in the method of presentation of analytical data. An "Analytical Guide," which comprehensively summarizes the possible sources of error and the methodological standard procedures, would be most helpful for investigating conservators.

References

- Aitken, M. J. (1961) Physics and Archaeology. New York: Interscience Publishers. 162-165.
- Baer, N.S. and Low, N.J.D. (1982) "Advances in Scientific Instrumentation for Conservation: An Overview," in Science and Technology in the Service of Conservation, Preprints of the Contributions to the Washington Congress, IIC, Washington 1982: 1-4.
- Brown, P.D.C. and Schweizer, F. (1975), "X-Ray Fluorescent Analysis of Anglo Saxon Jewellery," Archaeometry 15, Part 2: 175-192.
- Caley, E.R. (1965) "Critical Evaluation of Published Analytical Data on the Composition of Ancient Materials," in Application of Science in Examination of Works of Art, Proceedings of the Seminar conducted by the Research Laboratory, Museum of Fine Arts, Boston, Mass., September 1965: 167-171.
- Carter, G.F. (1964) "Preparation of Ancient Coins for Accurate X-Ray Fluorescence Analysis," Archaeometry 7: 106-113.
- Charles, J.A. (1973) "Heterogeneity in Metals," Archaeometry 15, Part 1: 105-114.

- Condamin, J. and Picon, M. (1965) "Notes on Diffusion in Ancient Alloys," Archaeometry 8:110-114.
- Cope, L.H. (1973) "The Metallurgical Examination of a Debased Silver Coin of Maximus Daza," Archaeometry 15, Part 2: 221-228.
- Dozinél, Ch.M. (1963) Modern Methods of Analysis of Copper and its Alloys. New York: Elsevier Publishing Company, 70.
- Emeleus, V.M. (1958) "Neutron Activation," Archaeometry 1:6-15.
- Glazunov, A. (1929) "Eléctrographie," Chimie et Industrie, Numéro spécial.
- Hall, E.T. (1953) "Analysis of Archaeological Specimens" in Times Science Review, No. 9: 13-14. See: IIC Abstracts 1956, Vol. 1, No. 3, 578.
- Hall, E.T. (1958) "Some uses of Physics in Archaeology," in Application of Science in Examination of Works of Art, Proceedings of the Seminar Conducted by the Research Laboratory, Museum of Fine Arts, Boston Mass., September 1958: 181-193.
- Hall, E.T. (1960). "X-Ray Fluorescence Analysis Applied to Archaeology," Archaeometry 3: 29-35.
- Hall, E.T. (1961). "Surface-Enrichment of Buried Metals," Archaeometry 4: 62-66.
- Hall, E.T. and Roberts, G. (1962) "Analysis of the Moultsford Torc," Archaeometry 5: 28-32.
- Hall, E.T. (1963). "Methods of Analysis (Physical and Chemical) Applied to Paintings and Antiquities," in Recent Advances in Conservation, Contributions to the IIC Rome Conference, 1961, ed. G. Thomson, London, Butterworth, 29-32.
- Hermann, H.W. and Wadlow, H.V. (1951) "Electrography and Electro-Spot Testing," Physical Methods in Chemical Analysis, Vol. 2, New York.
- Jánoska, P. (1987) "The importance of Material Testing: Restoration of a Roman Harness," Report, Eighth Triennial Meeting of the International Council of Museums Committee for Conservation, Sydney, September, 1987.
- Jedrzejska, H. (1962) "Sampling Precautions in the Analysis of Metallic Antiquities," Studies in Conservation 7, no.1: 27-32.
- Jedrzejska, H. (1972) "Analytical Problems in a Museum Laboratory (non-ferrous metal artifacts) Report, Third Triennial Meeting of the International Council of Museums Committee for Conservation, Madrid, September, 1972. See AATA, Supplement, "ICOM Reports on Technical Studies and Conservation," Vol. 14, no. 2 (1977), H/266.
- Jedrzejska, H. (1981), "Comments on X-Ray Fluorescence Quantitative Analyses of Ancient Silver Alloys," Report, Sixth Triennial Meeting of the International Council of Museums Committee for Conservation, Ottawa, September, 1981; 23/2.
- Laver, M. (1978) "Spot tests in Conservation: Metals and Alloys," Report, Fifth Triennial Meeting of the International Council of Museums Committee for Conservation, Zagreb, October 1978: 23/8.
- Mairinger, F. and Schreiner, M. (1982) "New Methods of Chemical Analysis - a Tool for the Conservator," in Science and Technology in the Service of Conservation, Preprints of the Contributions to the Washington Congress, IIC, Washington 1982: 5-15.
- Metcalfe, D.M. and Schweizer, F. (1971) "The Metal Content of the Silver Pennies ..." Archaeometry 13, Part 2: 177-190.
- Organ, R.M. (1962) "Are Analyses of Uncorroded Ancient Alloys Representative?" Studies in Conservation 9, no. 1 48-55/

- Pearson, C. (1988). "Conservation of Ethnographic Metal Objects," in The Museum Conservation of Ethnographic Objects, Senri Ethnological Studies no 23 (1988), National Museum of Ethnology, Osaka, 174-6.
- Sayre, E.V. and Meyers, P. (1971), "Nuclear Activation Applied to Materials of Art and Archaeology," Appendix, AATA 8, no. 4.
- Wawrzyczek, W. (1959) "Metoda Elektrograficzna i jej Zastosowanie w Chemii," (The Electrographic Method and its Application in Chemistry), Wiadomosci Chemiczne XII: 359-367.
- Young, W.J. (1963), "Application of the Microbeam Probe and Micro X-rays in Non-destructive Analysis," in Recent Advances in Conservation, Contributions to the IIC Rome Conferences (1963), ed. G. Thompson, London, Butterworth, 33-378.

Warsaw, November 1989

ABSTRACT

The treatment of corroded copper, brass and bronze ship fastenings often presents conservators with widely different responses from apparently similar or identical materials. This study demonstrates that the electrochemical techniques of measuring the polarization resistance and corrosion potentials of objects are powerful tools in resolving the differences in materials performance. The effects of sea water agitation, pH and dissolved oxygen on the above corrosion parameters are discussed. In the absence of any discernable differences in chemical composition, widely divergent corrosion rates can be rationalized in terms of the metal microstructure and the stresses induced at manufacture or during the shipwrecking process.

KEYWORDS

Composition, microstructure, copper, alloys, corrosivity, chloride.

THE EFFECTS OF COMPOSITION AND MICROSTRUCTURE ON THE CORROSIVITY OF COPPER ALLOYS IN CHLORIDE MEDIA

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Introduction

Despite the plethora of papers that deal with corrosion of copper and its alloys in chloride media the research relates primarily to materials of high purity and well defined composition.^{1,2,3} Conservators often find it difficult to bridge the gap between these model systems and the decaying artefact which they have just been told to conserve. Objects recovered from both land and maritime archaeological sites often present the worst cases of corrosion and are the most difficult to stabilize.⁴

In an attempt to overcome this conundrum the Western Australian Museum has carried out corrosion and conservation research on artefacts recovered from the historic shipwrecks off our coast which date back to the wreck of the *Trial* in 1622. The work of North and Pearson^{5,6,7} is notable for the characterization of corrosion mechanisms of iron and for new treatments to conserve these highly degraded objects. More recently the on-site measurements of corrosion potentials and surface pH of corroding iron objects has provided details of corrosion mechanisms on the seabed and a potential method for dating archaeological iron.^{8,9} Similar studies on copper and its alloys have also been reported.^{10,11}

A vast number of fastenings made of copper, brass and bronze have been recovered from the wrecks of the *Rapid* (1811), *James Matthews* (1841)¹² and *Eglinton* (1852). A wide range of apparent long-term corrosion rates were observed on the artefacts during conservation treatment. Sometimes the materials were very similar in composition and yet they presented different problems. Many of the difficulties could be rationalized in terms of the micro-environment^{13,14} and the gross differences in site conditions - the *James Matthews* is anaerobic and buried under several metres of sand while the *Rapid* and *Eglinton* lie in shallow reef strewn waters at depths from 8 to 4 metres. This work is an extension of the previous studies which concentrated on the effects of microstructure on corrosion and on the industrial archaeology that could be revealed.^{15,16}

This paper is an attempt to link traditional conservation techniques of metallographic and chemical analysis of artefacts with electrochemical parameters obtained on the same objects. Since impurities such as arsenic, antimony and bismuth commonly occur in copper and its alloys, a knowledge of the concentration and distribution in the parent metals can help explain the reasons why artefacts recovered from the same micro-environment will corrode at a different rate.¹⁷

This study reports on the effects of oxygenation on corrosion potentials (E_{corr}) and the initial corrosion rates of ships fastenings in sea water. Electrochemistry when used in conjunction with metallography provides conservators with an invaluable tool in the search for new understanding.

Experimental

The nine spikes and nails were examined metallographically after they had been sectioned and embedded in Araldite D or in Bakelite. Surfaces were prepared by grinding with wet and dry carborundum paper to 1200 grit and polishing with diamond paste to $\frac{1}{2}$ micron; the etchant was 2 wt% ferric chloride in ethanol. Larger objects, up to 60cm long, were sampled in six places with three longitudinal (LS) and three transverse sections (TS) representing the tail (shank), body and head regions of the fittings. Where the spikes had been broken in the shipwreck itself only four sections were taken since the tail of the fitting remained on site in the hull timbers. Smaller objects such as nails, up to 15cm long, were sectioned in four ways; a longitudinal section at the tip, transverse sections in the middle of the body and under the head and a longitudinal section of the head. The sections are labelled according to the diagram illustrated in fig. 1.

Drilled core samples (360 ± 100 mg) were taken from each object and dissolved at room temperature in 10% nitric, 5% hydrochloric and 2% tartaric acids to avoid volatilisation of antimony. Core samples were taken in an attempt to overcome the problems associated with analysis of archaeological metals.¹⁸ The alloys left no insoluble residues and the solutions were analysed using a Varian AA4 Spectrophotometer, except for arsenic which was determined commercially (ANALABS) by hydride generation. The results of the analyses are listed in Table I.

Vickers microhardness measurements on the polished sections were made using a Tukon Model 300 operating on a 400 gram load with a $\times 10$ objective; grain sizes were measured with the same instrument or by the ASTM method using a metallurgical microscope. Several sections were examined under the scanning electron microscope at CSIRO Division of Mineralogy using the back scattered

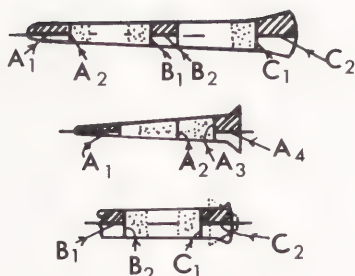


Fig. 1: Sectioning diagram for ships' fastenings.

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electron/low vacuum mode. Qualitative elemental analyses were done using the EDAX attached to the JSM2.

Electrical connections to the polished metal sections were effected by drilling through the plastic mounting resin and either soldering an insulated multi-strand copper cable to the rear of the section or by using electrically conducting epoxy resin. The cavity was then sealed with Araldite epoxy resin. The corrosion potentials were measured using a Metrohm calomel electrode (saturated with KCl) which was calibrated against a platinum electrode in a quinhydrone solution at pH 4.0. Voltages referred to in this paper are all relative to the saturated calomel electrode (SCE) unless otherwise stated. The water temperature was $22.5 \pm 1.5^\circ\text{C}$. Dissolved oxygen measurements were made using an ICI oxygen meter (411) after correction for the salinity of the sea water (35.5 ppt). The sea water was filtered after collection from the ocean and was stored in a refrigerator when not in use. The current voltage curves for polarization resistance measurements were recorded using an AMEL 551 potentiostat with a platinum auxiliary electrode and an XY recorder - the current voltage data was collected over a range of $\pm 20\text{mV}$ around the corrosion potential (E_{corr}) with the voltage scanned at $\pm 2\text{mV/sec}$. The effects of dissolved oxygen, stirring, etc. on E_{corr} were determined using a Fluke 8010A digital multimeter. The measurements were made in a modified Metrohm polarographic cell which allowed side mounting of the metal sections.

Corrosion Potentials and Polarisation Resistance

When copper and its alloys are immersed in oxygenated sea water they will corrode at a rate that is dependent on their chemical composition, micro-structure and on the amount of dissolved oxygen.^{19,20} In aerated solutions the corrosion potential is the voltage of a corrosion cell consisting of the anodic (oxidation of metal) and cathodic (oxygen reduction) half cells. The corrosion rate at the corrosion potential is given by the corrosion current, i_{corr} , which is related to the polarisation resistance, R_p , via the expression

$$\left(\frac{\Delta E}{\Delta i}\right) \Delta E \rightarrow 0 = R_p = \frac{B}{i_{\text{corr}}}$$

The constant B can be calculated via Faraday's laws relating to weight loss data or it can be determined from analysis of electrochemical polarization data. In physical terms the value of B can be obtained from the Stern and Geary²¹ relationship.

$$B = \frac{b_a \cdot b_c}{2.303 (b_a + b_c)} = i_{\text{corr}} \cdot R_p$$

where b_a and b_c are the anodic and cathodic decadic Tafel slopes. The value of B used to calculate the corrosion current is that previously determined from corrosion of *Rapid* bronze fittings in sea water.²² Using the anodic Tafel slope b_a $46 \pm 2\text{mV}$ and the cathodic slope b_c of $56 \pm 3\text{mV}$ the value of B, using the formula above, is 11mV . Our calculated corrosion currents are based on measurements of R_p after 15-25 hours of exposure of the samples to sea water and as such they are approximately one order of magnitude too high²³ and should be regarded as initial corrosion rates, rather than average long-term values. Nevertheless, the corrosion currents provide a useful guide to the performance of the alloys.

Results and Discussion

The results of the polarisation resistance measurements on the mounted and polished sections are summarized in Table II. In order to facilitate comparisons the wet chemical analyses listed in Table I are shown in the same groupings. Since the R_p values are determined from the slopes of the current voltage curves as $(\Delta E/\Delta i) \Delta E \rightarrow 0$ they are naturally dependent on the surface area exposed to the sea water so the i_{corr} values have been standardized to $\mu\text{A.cm}^{-2}$ (using the given surface areas) to enable the various R_p values to be properly compared.

Copper:

The four spikes and nails appear to have essentially the same chemical composition since the differences in the analyses shown in Table I are only minor. However, when we look at the calculated i_{corr} values we see that RP 3074 and JM 150/T13 are clearly corroding at a much higher rate than JM 150/T6 and JM 160/T8 and that the fittings clearly fall into two categories as far as corrosion currents are concerned. The only systematic chemical difference between the four fittings lies in their bismuth impurity concentrations with the lower corrosion rates corresponding with higher bismuth levels in the parent metal. In order to understand the causes for the 370% difference in corrosion rate between the two sets of copper fastenings we must look at their microstructures.

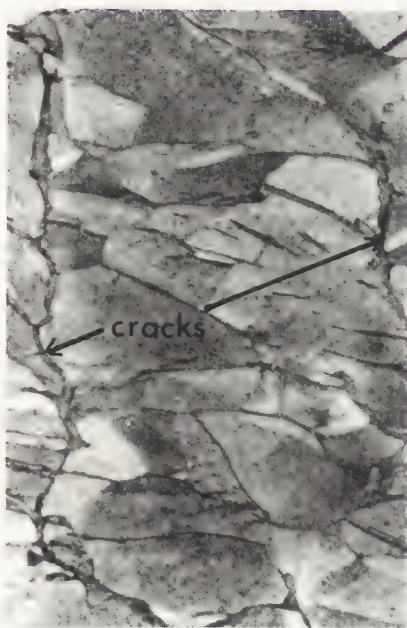


Fig. 2: Scanning electron micrograph of transcrystalline cracks and cold deformation of JM 150/T13 copper nail.
Full width 110µm.

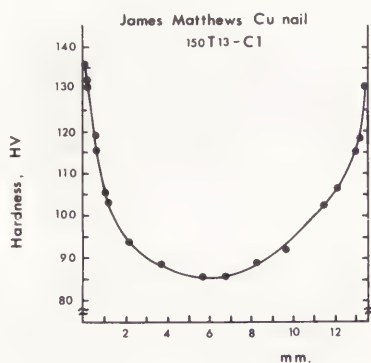


Fig. 3: Plot of the Vickers microhardness of the C1 transverse section of the JM 150/T13 copper nail.

The C1 transverse section of RP 3074 was taken just below the head of the spike whose structure is described as being a leaded arsenical copper with small amounts of tin, antimony, silver and bismuth and traces of iron and zinc. The microstructure of the spike is formed with fully recrystallized grains of the primary solid solution α . Over the whole volume numerous Cu_2O and Pb-rich particles were found. Their shape and density of distribution depend on degree of deformation (the distortion is only seen in longitudinal sections since their shape is circular in transverse sections). There are more cuprite (Cu_2O) inclusions than microdroplets of lead. The grains in the section are distorted as a result of cold-hammering of the head. The hardness at the edge of the section had a value of 134 which fell to $120 \pm 2\text{HV}$ in the centre. By way of contrast the middle of the shank, which is free of distortion, has a microhardness of 86HV.

The JM 150/T13 nail examined was also a transverse section below the head of the nail which is best described as an arsenical copper with a small amount (0.1 wt%) of lead (see Table I). The microstructure is similar to RP 3074 but it also has some Cu_2S inclusions as well as the Cu_2O and Pb inclusions previously noted. The nail has a clearly defined square head with bevelled edges and there are definite signs of transcrystalline cracks and cold deformation in the C1 section which was formed in the last stages of manufacture (see fig. 2). The hard working increases the hardness (HV) values from 86 for the fully recrystallized grains to a maximum value of 135. A typical plot of the way in which the hardness falls away with distance from the edge is shown in fig. 3. The higher corrosion rate of these two objects is probably a reflection of the stresses associated with the construction of the vessel (RP 3074) and the production of the nail itself (JM 150/T13). Increased corrosion rates as a result of surface strain and stress in copper has been the subject of intense study - annealing the metal causes a marked reduction in apparent corrosion rates.²⁴

By way of comparison we can look at the microstructure of the other two fittings from the *James Matthews* which corrode at a much lower rate. The spike, JM 150/T6, has a composition very similar to both the JM 150/T13 and the *Rapid* spike except that it has higher tin (0.41%), arsenic (0.41%) and bismuth (0.128%) impurity levels. The spike when recovered from the wreck site was broken in the middle of the body (see fig. 1). The centre sections of the spike consist of fully recrystallized grains of α solid solution with a small number of Pb-rich as well as Cu_2O and Cu_2S inclusions. Since the microstructure is essentially uniform, the spike has either been annealed after being cold-worked or it has been hot-worked. The microhardness of the B2 transverse section (see fig. 1) from the middle of the shank had maximum values at the edge (HV values 110 ± 2) which fell away to 86 ± 3 in the centre. The absence of highly stressed and distorted grains combined with the high levels of arsenic impurities have apparently provided a good combination for corrosion resistance. Electron microprobe analysis has shown that impurities such as As, Sb, Bi, etc. tend to concentrate along the grain boundaries²⁵ where their effective concentration is increased and so small levels of these impurities can have a marked effect on the materials performance. The high level of bismuth does lead to transgranular cracking in the head²⁶ during extensive working but this section was not the subject of our electrochemical analysis.

The *James Matthews* nail 160/T8 has a composition which is essentially the same as 150/T6 and T13 except that it has a much higher bismuth impurity level (0.255%). The microstructure is significantly different in that it consists of deformed grains of the α solid solution with inclusions of Cu_2O , Cu_2S and Pb-rich materials. The deformation of grains and the presence of bent twins proves that shaping of the fitting took place by cold-hammering. The deformation is most noticeable in the sections close to the tip since by the time we reach the C1 transverse section under the head the microstructure was surprisingly uniform with typical hardness values of $112 \pm 4\text{HV}$ across its breadth. The higher hardness is due to the higher levels of bismuth and arsenic and is not a reflection of stress.²⁷ The differences in the corrosion performance of these four copper fittings can be seen as being due to a combination of the microstructure (the stress, hardness, etc. associated with the experiences of the artefact from the time of manufacture, through shipwreck to recovery) and the amount of trace impurities such as arsenic and bismuth. The high levels of bismuth in the *James Matthews* made many of the spikes and bolts very tough but brittle and may have indirectly determined the fate of the vessel.

Brass:

Only two fittings were available for comparison, owing principally to the dates of manufacture of the vessels since in the early nineteenth century the majority of the fastenings were copper. The principal chemical difference between the *Rapid* brass spike and the *Eglinton* nail is that EG 1379 has 4.22% more zinc and that the *Rapid* spike is more heavily leaded (see Table I). The higher corrosion rate of the *Eglinton* brass, $28.3\mu\text{A.cm}^{-2}$ compared with $16.2\mu\text{A.cm}^{-2}$, is a little surprising since the increase of 16% in the amount of zinc has been translated into a 75% increase in corrosion. There are, however, very interesting differences in the metallurgical structures of the two samples, which help to explain the large increase.

The A₂ transverse section of RP 0000/T13 was made just under the head of the

spike. The spike has a high lead content (1.9%) and a small amount of tin (0.41%) as an impurity. The microstructure is formed with cored dendrites of primary α solid solution and a tin-rich phase which is present in interdendritic regions. Pb-rich particles are placed in interdendritic regions as well, individually or in association with tin-rich phases and their shape is most angular and they sporadically fill shrinkage cavities. The structure and colour of the spike is typical of a 70/30 brass with a small amount of Sn. The microhardness is greater closer to the surface with 160 \pm 10HV values occurring in the first 2mm in association with the tin-rich interdendritic phase; the mean hardness of the α cored (copper-rich) dendrites is 132 \pm 4HV. Because lead is the last component to solidify it tends to minimize the ingress of sea water through casting defects and thereby enhances the corrosion performance of the alloy.

The *Eglinton* 1379/T2 nail is a medium leaded 70/30 brass with a small amount of tin (0.29%). Apart from the higher zinc content its composition is remarkably similar to the *Rapid* spike. The microstructure is typical of a cast α brass (cored dendrites of α solid solution) which contains a small amount of the zinc-rich β phase in the interdendritic areas. In these areas Pb-rich particles are also found. The presence of "hot tear" fractures is probably due to premature removal of the nail from the mould when the β phase had not fully solidified. It is possible that the tear lines were not as deep as they currently appear but that the initial defect has been exacerbated by 125 years of corrosion. The crack has undergone extensive dezincification of the zinc-rich β phase. The normally beneficial effect of arsenic on dezincification has probably been masked by the relatively high level of iron (0.165%) as an impurity.²⁸ Microhardness measurements showed that C1 section had values that varied from 182HV for the equi-axed grains (40 \times 40 μ m) in the centre to 141HV to the columnar grains (104 \times 19 μ m) at the outer edge. The hardness varied in a linear fashion with increasing distance from the outer surface at the rate of 21 units per mm and is directly related to the grain shape and size. The higher corrosion rate of the *Eglinton* nail is directly related to the greater amount of zinc in the alloy since without the extra zinc there would have been insufficient β phase present to allow the "hot tear" to occur. The greater chemical reactivity of the zinc-rich β phase provides a greater driving force for interdendritic corrosion.

Bronze:

The deliberate addition of tin to copper has long been known to enhance the corrosion resistance of the alloy. Analysis of the three bronze nails (Table I) shows that the corrosion rates apparently mimic the amount of tin in the alloy, namely the higher the amount of tin, the lower is the apparent corrosion rate in the fully oxygenated sea water test solutions. The differences in corrosion rates are not due to a direct proportionality of composition but are also dependent on the microstructure of the bronzes.

The composition of the *James Matthews* 610 nail is, to say the least, highly unusual for a 19th century alloy. Although copper accounts for 90.74% of the weight, the tin content is only 3.60%. Apart from being a medium leaded bronze it also contains 0.84% bismuth, 1.396% arsenic and 2.32% nickel! (see Table I). The 25mm nail has an as-cast structure with the macrostructure consisting of a columnar zone and a couple of equi-axed relatively big grains in the centre of the nail. The microstructure, however, is typical of bronze containing higher amounts of tin (more than 10%) and has cored dendrites of primary α solid solution and a lot of islands of α plus δ eutectoid, which are placed in interdendritic areas. Pb-rich particles occur sporadically in the interdendritic areas with inclusions of zinc and lead sulphides. A lot of shrinkage cavities have been found in the transverse A_2 section near the head and there is 'tin sweat' under all of the surface. It would appear that the presence of the nickel, arsenic and bismuth (a total of 4.55 wt%) has dramatically changed the microstructure from that expected on the basis of the 3.6% tin. The microhardness at the tin-rich edge of the nail had values of 340! It is likely that the high bismuth, arsenic and nickel impurities came from a copper sulphide ore body that also contained minerals such as Parkerite ($\text{Ni}_3\text{Bi}_2\text{S}_2$) and Gersdorffite (NiAsS). Since silver sulphides are also found in association with these minerals it is not surprising that JM 610 has the highest silver content, 0.235 wt%, of the fifty copper alloys analysed in these laboratories. The presence of Cu_2S inclusions in the *James Matthews* copper fittings supports the use of a copper sulphide ore body as the source of the metal in France. The shrinkage in the alloy effectively increases the real surface area of the metal, thereby enhancing the corrosion rate.

The high leaded zinc bronze nail RP 3373B with 4.8 wt% zinc has a typical cast structure based on cored dendrites of the primary α solid solution. Given its higher tin content (5.53 wt%) it is not surprising to find many more light coloured islands of the α plus δ eutectoid (circular or angular in shape) than in the JM 610 bronze. There is rough gas porosity and shrinkage porosity over the transverse surface of the A_2 section (under the head of the nail) and this resulted from imperfect casting technology and would promote corrosion. There is a large area in the centre of the section with equi-axed grains. Tin-rich areas have been found in the interdendritic regions and there is also 'tin sweat' which results in a higher concentration of tin closer to the surface. The microhardness of the tin-rich areas was 178 \pm 6HV while the nickel-bismuth-arsenical bronze JM 610 had values as high as 340! In the middle of the section the hardness values were 120 \pm 5HV.



Fig. 4: Scanning electron micrograph of the RP 5004 bronze nail showing (light grey) islands of the α and δ eutectoid. Full width 190 μ m.

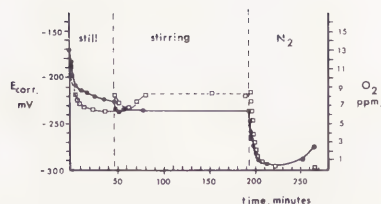


Fig. 5: Plot of the corrosion potential (mV vs SCE) and dissolved oxygen levels for the brass nail EG 1379/T2 in sea water as a function of time and water movement. ● = E_{corr} , □ = dissolved oxygen.

The leaded bronze nail RP 5004 had a tin content of 7.46 wt% and was essentially free of zinc (see Table I). The nail exists in its as-cast state and has not been mechanically worked or heat treated and it has a characteristic dendritic cast structure. The microstructure is very similar to RP 3373B with cored dendrites of α solid solution and particles of α plus δ eutectoid (see fig. 4). Lead-rich particles and sulphide inclusions occur sporadically in interdendritic areas. A lot of shrinkage and gas porosity have been found in the whole volume of the nail, which is proof again of imperfect foundry practice. Under the whole surface there are large amounts of tin-rich areas which were formed as a result of 'tin sweat'. Microhardness values of 184 \pm 4HV were found in the 'tin sweat' areas and the mean value of 138 \pm 7HV for the transverse sections is higher than that observed for the lower tin content of RP 3373B. The main effect of the greater tin content is to increase the "hard" zone around the edges from 200 μ m (RP 3373B) up to 1400 μ m in places.

Since there is no evidence of mechanical working in the three bronze nails there are no differences in corrosion rate due to stress. The inverse of the ratio of the amount of tin in the bronzes is 2.08:1.35:1.0 for JM 610:RP 3373:RP 5004 and the ratio of the initial corrosion currents is 2.54:1.39:1.0. The amount of tin in the bronze is obviously the dominant force in determining corrosion rates of the alloys in fully aerated sea water. The massive impurity levels (4.55 wt%) in the JM 610 nail and the 4.80% zinc in RP 3373B are apparently of secondary importance in determining the initial rates. However, the long-term corrosion rates may be significantly different.

Corrosion Potentials and Site Conditions

The determination of the corrosion potential of an artefact on the seabed or in the laboratory is readily achieved with a digital voltmeter, a reference electrode (calomel or Ag/AgCl) and a platinum electrode. Some archaeologists and conservators remain reserved in their judgement as to whether the various E_{corr} values mean anything. This section of the paper reports on a series of E_{corr} measurements on the artefacts in sea water where the effects of oxygen levels, stirring and pH were noted (see Table III). The data collected on representative samples of the alloys examined in the preceding section showed that the corrosion potential measurement by itself is very sensitive to changes in corrosion behaviour. The results are discussed under separate headings of copper, brass and bronze.

Copper: RP 3074 and JM 160/T8

The two copper samples showed up differences in their behaviour immediately after immersion in sea water. The more 'reactive' copper spike (see Table II) had a corrosion potential that rapidly changed with time. The E_{corr} of RP 3074 followed a $t^{1/2}$ dependence for twenty minutes with the potential being given by $E_{corr} = -0.144 - 0.0108 t^{1/2}$. The less reactive JM 160/T8 (see Table II) showed no rapid change in the same situation when the as-polished metal sections were first exposed to oxygenated sea water. No significant differences in behaviour of the two copper fittings were observed during the stirring of the solution or during deoxygenation. Stirring was effected by a magnetic follower and de-aeration was achieved with a bubbling stream of oxy-free nitrogen. The greatest fall in corrosion potential occurred in the 7-10 minutes it took to lower the dissolved oxygen level from 6.8 \pm 0.2 to zero ppm. Assuming that the corrosion potentials are in a region where there is a linear relationship between $\log i_{corr}$ and E_{corr} , the 26mV fall for RP 3074 would indicate that the corrosion rate had fallen by a factor of 3 and the 40mV fall for JM 610/T8 gives a five fold decrease. These calculations are based on the mean value of 56mV for the Tafel decadic slope for oxidation of copper alloys in sea water.²

Brass:

The E_{corr} of the RP 0000/T13 brass spike was essentially independent of the time spent sitting in sea water and didn't change with stirring. Deoxygenation of the solution caused the E_{corr} to fall initially by 18mV but the E_{corr} gradually drifted back to its initial value of -0.226 volts which may indicate a change-over in corrosion mechanism, i.e. instead of the copper-rich phases corroding under oxygenated conditions the zinc-rich dendrites can corrode preferentially at low oxygen potentials.

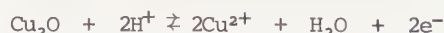
The more reactive brass sample, EG 1379/T2, showed a marked time dependence of the corrosion potential that was largely determined by the dissolved oxygen level (see fig. 5). During the initial immersion in sea water the concentration of oxygen fell from 11.8 to 6.3 ppm and the E_{corr} fell by 62mV according to the equation $E_{corr} = -0.192 - 0.021 \log t$, for 45 $\leq t \leq 5$ minutes. Stirring had little effect on the E_{corr} . During degassing with nitrogen the E_{corr} again fell logarithmically with time with $E_{corr} = -0.250 - 0.046 \log t$, for 7 $\leq t \leq 2$ minutes and a total fall of 67mV (see Table III). On standing for 24 hours the dissolved oxygen level had returned to 8.3 ppm and E_{corr} returned to the same value (-0.211 volts) it had during the initial immersion.

Using the decadic Tafel slope of 56mV we can calculate that the decrease in E_{corr} of 18mV on deoxygenation for RP 0000/T13 corresponds to a two-fold reduction in corrosion rate while the 67mV change for EG 1374/T2 implies a fall in corrosion rate by a factor of almost sixteen.

Bronze:

The arsenical bronze nail JM 610 showed the same dependence of E_{corr} on standing in sea water as the brass nail from the *Eglinton* with E_{corr} being given by the relationship $E_{\text{corr}} = 0.168 - 0.019 \log t$ as the oxygen concentration fell from 5.5 ppm to 4.2 ppm. The plateau value of -0.191 was reached after 45 minutes. Stirring the solution had no effect. E_{corr} fell by a further 53mV after degassing with oxy-free nitrogen for ten minutes. The same behaviour of the arsenical bronze JM 610 and the *Eglinton* brass nail is seen in not only the same response of E_{corr} to oxygen (see Table III) but also in the same calculated i_{corr} values for oxygen saturated sea water since 28.3 and 29.2 $\mu\text{A}/\text{cm}^2$ are well within the 13% reproducibility range of the Rp data.

Addition of HCl to the sea water changed the E_{corr} and the pH of the solution in accordance with the redox equilibrium.



where the voltage is given by $E_{\text{NHE}} = 0.203 + 0.0591\text{pH} + 0.0591 \log \text{Cu}^{2+}$.³⁰

The E_{corr} of the high leaded zinc bronze nail RP 3373B decreased on standing in sea water according to the relationship $E_{\text{corr}} = -0.175 - 0.0098 \log t$ until it reached a plateau value of -0.186 volts. The corrosion potential was significantly affected by stirring, with E_{corr} falling to -0.221 volts after 50 minutes. Degassing the sea water saw E_{corr} fall by a further 132mV after one hour, but then the voltage gradually rose to -0.324 volts after six hours at zero oxygen concentration. Such behaviour is consistent with a changeover from corrosion of the copper-rich α phase in oxygenated sea water to corrosion of the tin-rich $\alpha + \delta$ eutectoid phase. The response of E_{corr} to changes in pH on addition of HCl to the sea water solution was the same as that observed for JM 610.

The response of the leaded bronze nail RP 5004/T11 to immersion in sea water was minimal in that the corrosion potential didn't change after standing for an hour or being stirred for half an hour. The lack of response is consistent with this bronze having a high resistance to corrosion. Degassing with nitrogen saw the potential fall to a minimum value of -0.235 after 36 minutes (see Table III) before it gradually rose, at zero ppm dissolved oxygen, to -0.213 after 15 hours. The change in E_{corr} on standing under nitrogen is very similar to the high leaded zinc bronze RP 3373B.

Inspection of the data listed in Table III of the maximum change in E_{corr} on deoxygenation, prior to any changeover of mechanism, indicates that the leaded zinc brass nail RP 3373B was the most sensitive to changes in corrosion rate. The calculated decrease in corrosion rate for this nail was a factor of 227 while the decrease for the nickel-bismuth-arsenical bronze JM 610 was almost 9 and the decrease for the high bronze nail RP 5004 was almost six fold.

Conclusion

Electrochemical measurements on a range of copper, brass and bronze fittings have shown that reproducible values of the corrosion currents (i_{corr}) deduced from polarisation resistance data provide an insight into the stability of artefacts. Apparently anomalous differences in i_{corr} values can be understood in terms of the microstructure and microhardness of the metals and the effect of impurities. The proportions of the major alloying elements of tin and zinc generally dominate the corrosion performance of the fastenings. This work has shown that the corrosion potential, E_{corr} of the artefacts is very sensitive to changes in corrosion brought about through differences in composition, mechanical stress and oxygenation. Simple measurement of the corrosion potential of artefacts can provide the conservator with a useful guide as to which object is the most unstable and therefore in most need of urgent treatment.

Acknowledgements

We are happy to acknowledge the help of our co-worker Maria Pitrun who performed the metallographic analyses. Thanks also go to Bruce Robinson at CSIRO, Floreat, for access to the SEM and to Terry Pile at Curtin University of Technology for use of the microhardness instruments.

References

1. P.T. Gilbert, (1982), "A Review of Recent Work on Corrosion Behaviour of Copper Alloys in Sea Water", *Materials Performance*, 21:47-53.
2. W.S. Bjorndahl and K. Nobe, (1984), "Copper Corrosion in Chloride Media: Effect of Oxygen", *Corrosion*, 40(2):82-87.
3. E.D. Mor and A.M. Beccaria, (1979), "Effects of Temperature on the Corrosion of Copper in Sea Water at Different Hydrostatic Pressures", *Werkstoffe und Korrosion*, 30:551-558.

4. R.F. Tylecote, (1979), "The Effects of Soil Conditions on the Long-Term Corrosion of Buried Tin-Bronzes and Copper", *J. Archaeological Science*, 6:345-368.
5. N.A. North, (1982), "Corrosion Products on Marine Iron", *Studies in Conservation*, 27:75-83.
6. N.A. North and C. Pearson, (1978), "Washing Methods for Chloride Removal From Marine Iron Artefacts", *Studies in Conservation*, 23:174-186.
7. N.A. North and C. Pearson, (1978), "Methods For Treating Marine Iron", *ICOM Committee For Conservation, 5th Triennial Meeting, Zagreb*, 78/23/30:1-10.
8. I.D. MacLeod, (1981), "Shipwrecks and Applied Electrochemistry", *J. Electroanal. Chem.*, 118:291-303.
9. I.D. MacLeod, (1989), "The Electrochemistry and Conservation of Iron in Sea Water", *Chemistry in Australia*, 56(17):227-229.
10. I.D. MacLeod, (1989), "Marine Corrosion on Historic Shipwrecks and its Application to Modern Materials", *Corrosion Australasia*, 14(3):8-14.
11. R.J. Taylor and I.D. MacLeod, (1985), "Corrosion of Bronzes on Shipwrecks - a Comparison of Corrosion Rates Deduced From Shipwreck Material and From Electrochemical Methods", *Corrosion*, 41(2):100-104.
12. G.J. Henderson, (1980), "Unfinished Voyages: Western Australian Shipwrecks 1622-1850", University of Western Australia Press, p.182-184.
13. I.D. MacLeod and N.A. North, (1980), "350 Years of Marine Corrosion in Western Australia", *Corrosion Australasia*, 5:11-15.
14. I.D. MacLeod, (1985), "The Effects of Concretion on The Corrosion of Non-Ferrous Metals", *Corrosion Australasia*, 10(4):10-13.
15. I.D. MacLeod and M. Pitrun, (1986), "The Effects of Microstructure on Long-Term Corrosion", Symposium 11, Lead Paper, *Proceedings of Conference 26, Adelaide, November*. Australasian Corrosion Association, Vol. II.
16. I.D. MacLeod and M. Pitrun, (1988), "Metallography of Copper and its Alloy Recovered from Nineteenth Century Shipwrecks", *Archaeometry: Australasian Studies*, Ed. J. Prescott, Dept. of Physics, University of Adelaide, Australia.
17. M.J. Pryor and K.K. Giam, (1982), "The Effects of Arsenic on the Dealloying of α - Brass", *J. Electrochem. Soc.*, 129(10):2157-2164.
18. E.R. Caley, (1964), "The Heterogeneity of Ancient Metals and the Sampling Problem", in *Analysis of Ancient Metals*, Pergamon Press, London, p.1-15.
19. P.T. Gilbert, (1982).
20. W.S. Bjorndahl and K. Nobe, (1984).
21. M. Stern and A.L. Geary, (1957), "Electrochemical Polarization I - A Theoretical Analysis of the Shape of Polarization Curves", *J. Electrochem. Soc.*, 104:56-63.
22. R.J. Taylor and I.D. MacLeod, (1985).
23. B.C. Syrett and D.D. MacDonald, (1979), "The Validity of Electrochemical Methods for Measuring Corrosion Rates of Copper-Nickel Alloys in Sea Water", *Corrosion*, 35(11):505-509.
24. D. Lewis, D.O. Northwood and C.F. Pearce, (1969), "Copper Microstrain and Electrode Potential", *Corrosion Science*, 9(10):779-787.
25. K. Oishi, T. Tsuji and Y. Watanabe, (1982), "Behaviour of Various Elements in Dezincification Layer Examined by Means of X-ray Micro-Analyser (XMA)", 'Proc. Int. Symp. Corros. Copper and Copper Alloys in Buildings', JCDA, Tokyo, p.256-269.
26. S.L. Archbutt and W.E. Prytherch, (1937), "Bismuth-arsenic-antimony-nickel oxygen", Chapter 8 from 'Effects of Impurities in Copper', Res. Monograph 4, British Non-Ferrous Metals Res. Assn., London, p.96-109.
27. Idem.
28. K. Oishi, T. Tsuji and Y. Watanabe, (1982).
29. R. Grauer, P.J. Moreland and G. Pini, (1982), "A Literature Review of Polarisation Resistance Constant (B) Values for the Measurement of Corrosion Rate", NACE, Houston, Texas.
30. M. Pourbaix, (1974), "Atlas of Electrochemical Equilibria in Aqueous Solutions", 2nd Ed. NACE, Houston, Texas, p.386.

Table I: Composition of Ships' Fastenings, wt%

	Reg. No.	Cu	Sn	Zn	Pb	Sb	Ni	Ag	Fe	As	Bi
<u>Copper:</u>											
<i>Rapid</i> - spike	3074	98.14	0.0375	0.0022	0.163	0.024	0.018	0.088	0.003	0.21	0.047
<i>James Matthews</i> - nail	150/T13	98.38	0.049	0.0037	0.101	0.027	0.021	0.108	0.002	0.34	0.077
<i>James Matthews</i> - spike	150/T6	98.60	0.41	0.0033	0.0097	0.022	0.050	0.078	0.002	0.42	0.128
<i>James Matthews</i> - nail	160/T8	98.63	0.074	0.0025	0.109	0.009	0.047	0.104	0.002	0.29	0.255
<u>Brass:</u>											
<i>Rapid</i> - spike	0000/T13	70.04	0.32	26.39	1.90	0.049	0.074	0.078	0.165	0.022	0.014
<i>Eglinton</i> - nail	1379/T2	68.54	0.29	30.61	0.61	0.008	0.058	0.059	0.165	0.068	0.082
<u>Bronze:</u>											
<i>James Matthews</i> - nail	610	90.74	3.60	0.044	0.55	0.135	2.32	0.235	0.039	1.39	0.84
<i>Rapid</i> - nail	3373B	84.43	5.53	4.80	3.76	0.141	0.064	0.111	0.244	0.29	0.025
<i>Rapid</i> - nail	5004/T11	90.3	7.46	0.024	0.81	0.545	0.086	0.151	0.086	0.042	0.231

Table II: Polarisation Resistance Values and Corrosion Currents* for Copper Alloys in Sea Water

	Reg. No.	Surface area cm ²	R _p ohm	i _{corr} μA/cm ²
<u>Copper:</u>				
<i>Rapid</i> - spike	3074	0.788	465	29.9
<i>James Matthews</i> - nail	150/T13	1.68	220	29.8
<i>James Matthews</i> - spike	150/T6	2.45	550	8.1
<i>James Matthews</i> - nail	160/T8	1.38	957	8.2
<u>Brass:</u>				
<i>Rapid</i> - spike	0000/T13	1.0	675	16.2
<i>Eglinton</i> - nail	1379/T2	0.33	1187	28.3
<u>Bronze:</u>				
<i>James Matthews</i> - nail	610	0.25	1500	29.2
<i>Rapid</i> - nail	3373B	0.29	2375	16
<i>Rapid</i> - nail	5004/T11	0.20	4650	11.5

*Note: All corrosion currents are approximately one order of magnitude higher than typical long-term values owing to the short equilibrium times used in this experiment.¹¹ The dissolved oxygen level was 17.2 ppm with flowing sea water stirred by a magnetic follower and bubbling oxygen.

Table III: Corrosion Potentials of Copper, Brass and Bronze Fittings in Sea Water*

	Initial	Rest	Stirred	Deoxygenated	$\Delta O_2 - N_2^a$ mV
<u>Copper:</u>					
RP 3074	-0.144	-0.199	-0.212	-0.238	-26
JM 160/T7	-0.188	-0.183	-0.204	-0.244	-40
<u>Brass:</u>					
RP 0000/T13	-0.218	-0.218	-0.226	-0.244	-18
EG 1374/T2	-0.164	-0.226	-0.235	-0.302	-67
<u>Bronze:</u>					
JM 610	-0.174	-0.191	-0.193	-0.246	-53
RP 3373B	-0.170	-0.186	-0.221	-0.353	-132
RP 5004/T11	-0.191	-0.191	-0.192	-0.235	-43

*Voltages are measured relative to the saturated calomel electrode (SCE) whose potential was 0.244±0.002 volts vs NHE.

^aThe values of $\Delta O_2 - N_2$ refer to the change in corrosion potential of the metals between equilibrium in the stirred oxygenated solution and after deoxygenation.

ABSTRACT

As a result of the research conducted, it is established that ancient granulated jewelry are made of silver (Ag) 960⁰⁰⁰ and gold (Au) - 750⁰⁰⁰ and higher. All the items under study are affected by intercrystalline corrosion. The solder which fuses the base with granules is especially subject to destruction. The alternative use of mechanical and chemical cleaning, together with heat treatment make it possible to achieve a comparatively stable crystalline structure of the metal (Ag, Au) and to turn the larger amount of the corrosion compound into silver (Ag) and copper (Cu) complementing the composition of the solder which fuses into it. It is defined that while soldering silver ancient master-craftsmen used the double alloy of silver-copper and the triple alloy of gold-silver-copper. The technology of making granulated silver and gold is also presented.

KEYWORDS

Granulation, corrosion of metals, intercrystalline corrosion, recrystallization, reconstruction, soldering, the amalgam, "tinning", chemical and classical methods, restoration.

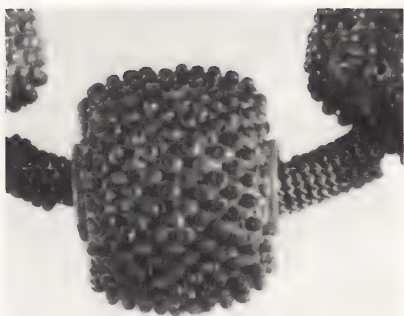


Fig.2. The three-bead pendant after restoration. Detail. Silver, granulation. Kievan Rus, 12th c. Enlarged 4 times

RESTORATION OF ANCIENT ARCHAEOLOGICAL GRANULATION JEWELRY

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Introduction

From ancient times, the art of making granulated jewellery was practiced in Egypt, Greece, Byzantium, Western Europe and Old Rus. This technique consists in working decorative gold or silver, so that the metal forms into tiny spheres which create a granulated surface in the forms of triangles, rhombuses or nets. Sometimes, the work is densely covered with granules set in strict rows, each granule placed upon a separate tiny ring, almost microscopic in size - this technique makes the work especially delicate with the interplay of light and shade.

An unsurpassed example of mastership attained by antique craftsmen is presented by the earrings from Feodosia (4th century B.C., the Hermitage). The size of granules does not exceed 0.17 mm. The art of granulation was extensively practiced in the territory of the present-day Ukraine and Russia prior to the Mongol invasion. The museums of this country keep many works of granulated jewellery.

Until recently the research of granulated silver and gold was exclusively of theoretical nature. The restorers were extremely wary of doing harm to these brittle works intricate as to the technique employed. The restoration work was limited by the clearing of the articles from traces of soil and subsequent conservation. The granulated articles showed numerous traces of crumbling during the process of cleaning and preservation due to the destruction.



Fig.1. Treasure trove of gold and silver jewellery, 11th-13th cc. Found by A. Manchuk in 1986, Kiev. Kept in the Ukrainian SSR State Museum of History



Fig. 4. Corrosion of the soldered joint. Enlarged 100 times. A granule of the bead. Silver. Kievan Rus. 12th c.



Fig. 3. Jewelry articles of the 11th-12th cc. after restoration from the museums of the Ukraine

A new stage in the research of granulated jewelry is associated with the name of Irina Ravich, Candidate of Sciences (Engineering) who some years ago started conducting the research at the USSR Institute of Restoration. Her work allowed to establish a new trend and to tackle a number of problems. Her experiments in recrystallization of archaeological silver affected by intercrystalline corrosion on the example of the granulated beads (Smolensk) proved especially valuable. Her conclusions greatly contributed to the further development of this trend in the research.

Research

In 1986-1989 we carried out the research of granulated jewelry with granules of some 0.6-2.0 mm dating to the 6th-13th centuries from Kiev treasure trove (1986), see Figs. 1,2; as well as from art museums of Chernigov, Kharkov, Khmel'nitsky. The jewellery includes the three-bead pendants of "Kiev type", pendants from Great Moravia, agraffes, colts, hinged bracelets of the period of Kiev Rus and Avarian belts. (See Figs 3,10.)

The spectral, metallographic and analytical methods of scientific research have allowed to determine the composition of alloys, solder and products of corrosion. For the most part, granulated jewelry is made of the double alloys of silver-copper with the silver content from 90% to 96% for silver articles; and double and triple alloys of gold-silver-copper with the content of gold from 75% and more for gold granulation work.

For soldering silver the double alloy of silver-copper with the silver content from 72% to 80% is used. For soldering gold items, the triple alloy of gold-silver-copper is used with the ratio of 60%-20%-20% for gold 750₀₀₀ and 80%-15%-5% for pure gold samples.

As a result of the protracted stay in the soil, high standard granulation silver from archaeological excavations are considerably affected by corrosion (see Figs 4,10). In salty soils the silver surface turns into AgCl (e.g., Avarian belts). As a rule, however, the articles under study are covered by Cu_2S , Cu_2O , Ag_2O , Ag_2S , Ag_2SO_3 , Ag_2CO_3 and by CuCO_3 , $\text{Cu}(\text{OH})_2$ and $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ at the solder joints.

To work out the methods of restoration of archaeological granulation silver, we had to thoroughly study the ancient technology of jewelry making (see Figs. 11-13). On the basis of our research we tried to master the ancient technique making use of the methods described in the works by Theofilus[1], M. Rosenberg[2], E. Brepohl [3] and F. Mishukov[4].

As a result of numerous attempts and with the help of modern technical means, as well as the methods available to



Fig. 5. Bead. 12th c. Detail. Prior to the cleaning. Enlarged 35 times

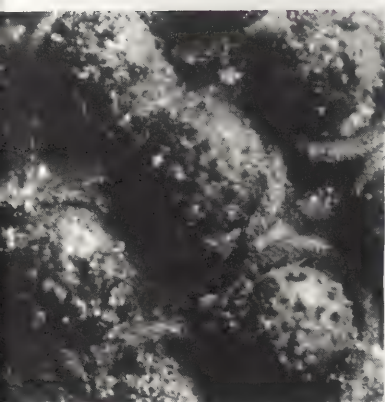


Fig. 6. Detail. After removing the soil, washing and chemical treatment. Enlarged 35 times

ancient masters, the satisfactory results have been attained.

We propose 4 methods of piling up the solder and soldering granules which proved quite satisfactory. (See Figs. 14, 15, 16, 17)

Restoration

The experience and know-how the author acquired while restoring granulated jewellery has enabled him to work out the unique methods of restoration archaeological granulated articles. The method is based on the successive use of mechanical, chemical and heat treatment. Their succession depends upon the results of the analysis, the composition of corrosion and the degree of preservation.

As a rule, the work begins with mechanical clearing of the sample from the soil and loose corrosion layers, see Fig. 5. This is followed by the treatment of 10% water solution of sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$), then thorough washing in water, which is immediately followed by the treatment in sodium thiosulfite ($\text{Na}_2\text{S}_2\text{O}_3$) and washing in water again. As a result, corneous silver (AgCl) and copper salts are removed. (It must be borne in mind that CuCl demands local treatment in the saturated solution of ammonium (NH_3)). The treatment by ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) concludes the process. (See Fig. 6.)

The heat treatment at $t+400^\circ\text{C}$ - $+450^\circ\text{C}$ is carried out in the flame of a benzine blow lamp, the final decomposition of sulfides (Cu_2S ; Ag_2S) and carbonates (Ag_2CO_3) is determined by visual control, see Fig. 7. After that the sample is cleared with a brush to undergo the heat treatment anew with the aim of recrystallization of metal structure. For this purpose, the sample is put in the thin charcoal powder in the crucible and placed in the automatic muffle furnace to be kept there for 15 min at $t+650^\circ\text{C}$. Then the muffle furnace is switched off while the crucible is left there until it is cooled down. (See Fig. 8.)

The sample is cleaned again and very carefully at that, for after the removal of corrosion products, the soldering joints are very weak. We have glittering white metal with spots of dark copper oxides (CuO). The soldering presents the last stage of thermic treatment. If there is any need, you may now correct any deformation and restore details and fragments using water solutions of flux ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$). The sample is heated in the oxidized flame of a benzine blow lamp on the charcoal; at $t+850^\circ\text{C}$ copper oxides are reduced to pure copper (Cu) and fuse to powdery silver (Ag). Simultaneously, the original solder is at the stage of solidifying, it melts to form a fusible plate (zone) which joins granules and details. (See Fig. 9.)

The method is reliable and guarantees the thinnest zone of soldering. Some experience acquired, you run no risk of harming a monument of art.

In case the solder with large content of silver and copper is used for soldering, the above-mentioned method can also be acceptable for granulated gold. Such solder is also subject to corrosion which definitely weakens the soldering joints.

To protect archaeological finds which underwent the restoration according to the above-mentioned method, we recommend the passivation - 1% solution $\text{K}_2\text{Cr}_2\text{O}_7$, $t+20^\circ\text{C}$, time - 20 min.

Conclusions

The Programme of Restoration of Granulated Jewellery in a Fair State of Preservation

1. To assess the degree of preservation
2. To determine the degree of corrosion and its composition
3. To evaluate the structure of the alloys
4. To make the qualitative and quantitative analysis of alloys
5. Mechanical cleaning
6. Chemical cleaning and washing
7. Heat treatment, $t+450^\circ\text{C}$
8. Mechanical cleaning
9. Heat treatment, $t+650^\circ\text{C}$, 15 min
10. Mechanical cleaning
11. Restoring and enforcing soldering, $t+850^\circ\text{C}$
12. Cleaning, washing, drying out, defatting
13. Conservation

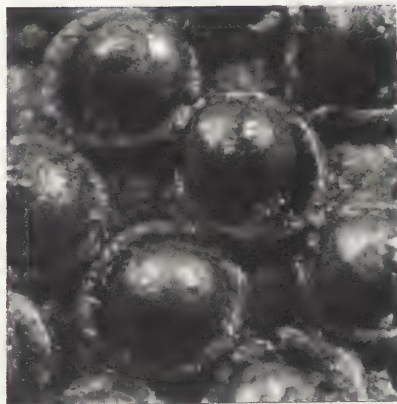


Fig. 7. Detail. After heat treatment, $t+450^\circ\text{C}$. Enlarged 35 times

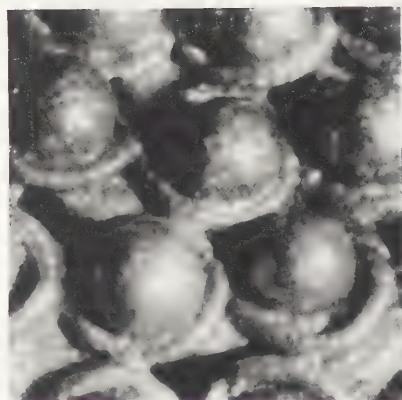


Fig. 8. Detail. After recrystallization, $t+650^\circ\text{C}$. Enlarged 35 times



Fig. 9. Detail. After the renovated soldering. Enlarged 35 times

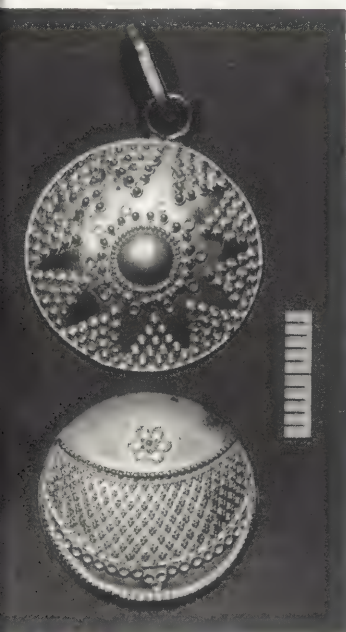


Fig. 12. The author's reconstruction of soldering of Old Rus and antique granulation. Enlarged 2.2 times

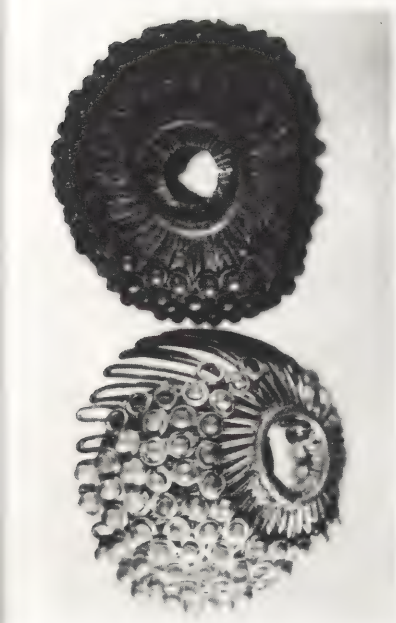


Fig. 13. A bead of the pendant, 12th c. Technology of its production. Author's reconstruction. Enlarged 5 times



Fig. 10. Plaque of the belt. Avarians, 6th c. Gold, silver, granulation. Details before and after restoration

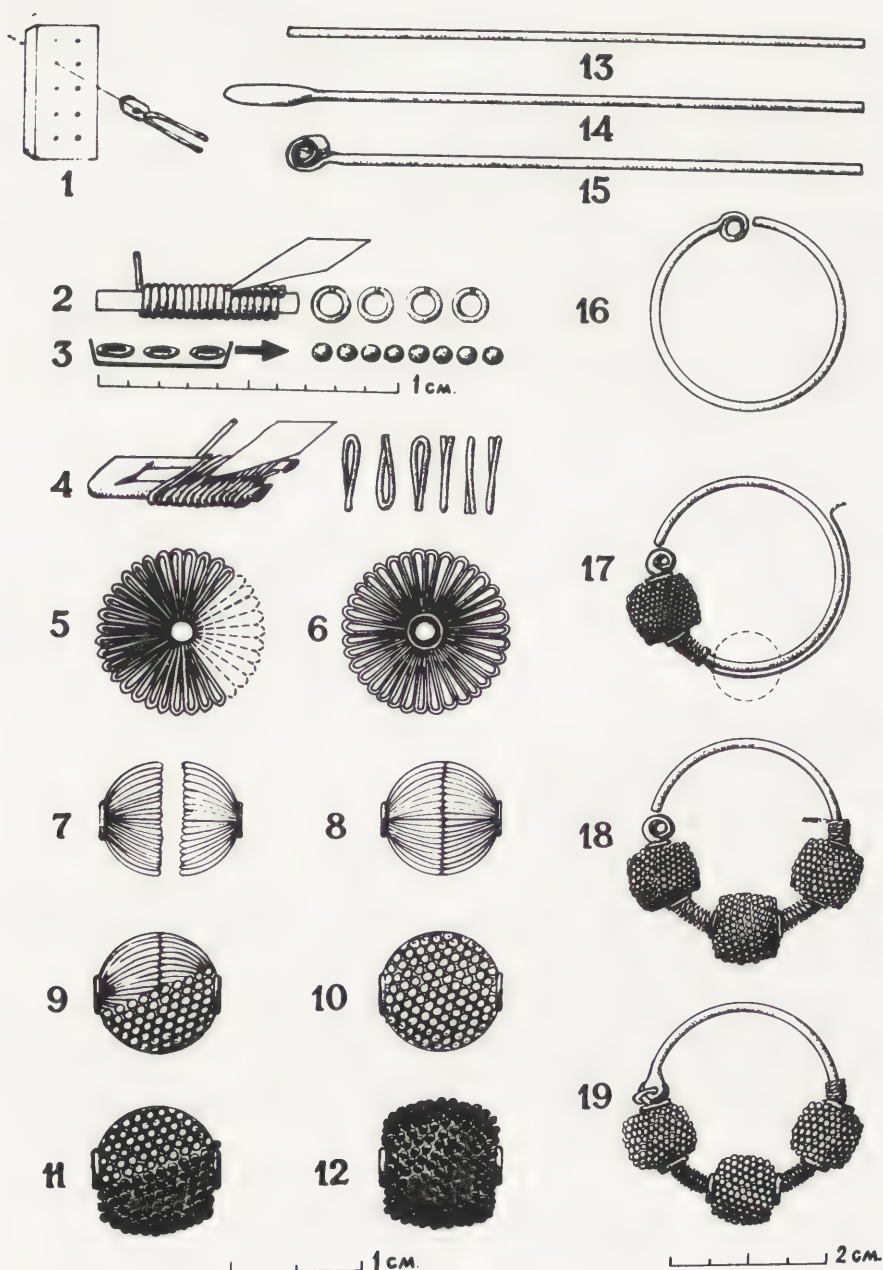


Fig. 11. Technology of making Old Rus three-bed pendants from Kiev treasure trove (found in 1986). Soldering is used in positions 6, 8, 10, 12, 18



Fig.15. Soldering with the "tinning" method. Enlarged 23 times. Author's reconstruction

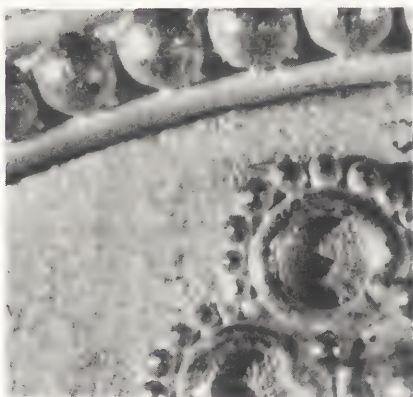


Fig.16. Soldering with the chemical method. Enlarged 25 times. Author's reconstruction



Fig.17. Soldering granulation work with the classical method. Author's reconstruction. Enlarged 15 times

The Methods of Soldering Granules ТЕХНОЛОГИЯ ПАЙКИ ЗЕРНИ

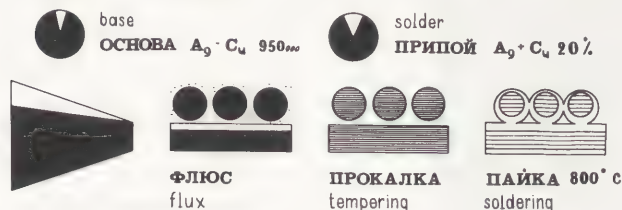
1 The Amalgam Method

1 АМАЛЬГАМНЫЙ МЕТОД



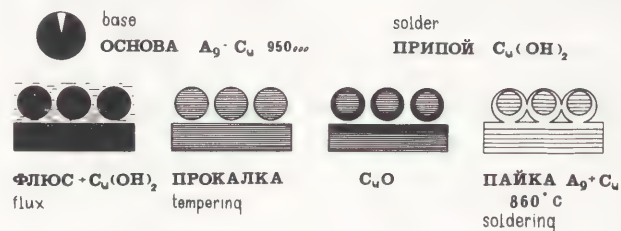
2 The "Tinning" Method /piling solders in a thin plate/

2 МЕТОД "ЛУЖЕНИЕ" (нанесение тончайшей плёнки припоя)



3 Chemical Method

3 ХИМИЧЕСКИЙ МЕТОД



4 Classical Method

4 КЛАССИЧЕСКИЙ МЕТОД

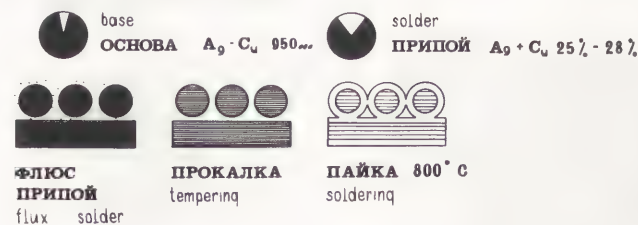


Fig.14. Methods of Soldering Granules

References

1. Theophilus Presbyter. *Schedula Diversarum Artium*. Budapest Műszaki Könyvkiadó, 1986; с. 94-97
2. Mare Rosenberg, *Granulation Geschichte der Goldschmiedekunst auf Technischer Grundlage*, F a/M, 1918, P.12-13
3. Ernard Brépohl, *Theorie und Praxis des Goldschmieds*. Leipzig: VEB Fachbuchverlag, 1962. pp. 256-261
4. Мишуков Ф.Я. Невидимый припой ювелиров древности. Труды МВХПУ, вып.2, 1962. с.4
5. Шемаханская М.С. Проблемы реставрации археологического металла /Информцентр по проблемам культуры и искусства МК СССР М., 1981. с.18-23

RESUME

A la suite d'observations réalisées sur des canons du XVIII^e siècle, conservés à Haïti, sur le site de la Citadelle Laferrière, l'auteur propose une technique de protection des objets métalliques fondée sur la création d'un couple galvanique.

MOTS-CLES

Climat tropical, conservation, couple galvanique, fer, protection cathodique.

LA PROTECTION DES GROSSES PIÈCES MÉTALLIQUES PAR CRÉATION D'UN COUPLE GALVANIQUE, AVENIR OU UTOPIE?

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FRANCE

Introduction

Dans le cadre d'une mission de consultant pour l'UNESCO, à Haïti, nous avons eu à intervenir sur du matériel métallique: 150 canons, des milliers de boulets et de nombreux restes de divers matériel militaire.

Tout ce matériel se trouve sur le site grandiose de la Citadelle Laferrière située au nord de Haïti, en pleine zone tropicale et proche de la mer. La Citadelle est située à environ 1000 mètres d'altitude et sa position en fait une barrière naturelle pour les brumes et les pluies chargées de sel marin. L'humidité relative est très importante tout au long de l'année et, par conséquent, les phénomènes de corrosion atmosphérique y sont intenses.

Notre intervention s'est déroulée en deux temps:

- une première période de trois semaines pour étudier le matériel et définir les techniques de traitement les mieux adaptées et effectuer quelques essais de conservation;
- une seconde période, six mois plus tard, pour vérifier l'évolution des traitements proposés, mettre en route l'atelier de conservation sur place, former les personnes chargées des travaux et réaliser le traitement d'une dizaine de canons et de quelques dizaines d'autres pièces métalliques.

1. Etude du matériel:

Les canons datent de la fin du XVIII^e siècle et proviennent de prises effectuées par la République de Haïti sur des vaisseaux français, britanniques et espagnols au moment de la guerre pour l'indépendance.

1.1. Les canons en bronze:

Ils ne présentent pas d'altération notable bien qu'ils soient posés directement sur le sol. Ceci peut s'expliquer, d'une part par la qualité du métal (bronze marine), mais aussi par la présence de très nombreux boulets de canon en fer restés coincés dans les fûts, endroit où s'accumule plus volontiers l'humidité. Le couple fer-bronze, ainsi créé, aurait permis la préservation du bronze au détriment des boulets qui sont, en effet, beaucoup plus abîmés que ceux restés à l'air libre. Nous nous trouvons dans le cas d'un couplage galvanique classique. Devant l'impossibilité matérielle de sortir les boulets contenus dans les fûts, nous avons décidé de conserver la protection galvanique existante.

1.2. Les canons en fer:

Nous pouvons les classer en deux catégories:

- ceux qui sont relativement bien conservés, remplis de boulets, eux aussi;
- ceux qui sont très abîmés et qui sont systématiquement pourvus d'une lumière en bronze qui, elle, est parfaitement conservée. Peut-on en conclure que le rapprochement de ces deux métaux a produit la destruction complète du fer alors que la lumière en bronze ne représente que 450 à 500 grammes de métal contre plusieurs tonnes (2,5 à 3,5T) de fer?

Il faut noter:

- 1° qu'il n'existe pas de catégorie intermédiaire à l'exception d'un seul canon;
- 2° que les canons corrodés et non corrodés sont issus d'une même fabrication en série.

Nous pensons, comme le souligne J. Galland (1) et, contrairement à ce qu'affirme M.J. Pryor (2) que ce phénomène peut, en effet, être à l'origine de la destruction du fer de certains canons, les autres étant bien conservés.

Nous serions bien là dans le cas d'une protection par rapprochement (3) et non d'une protection cathodique (4) qui nécessite un milieu aqueux ou gorgé d'eau qui n'implique pas le contact en court-circuit entre anode et cathode (5).

2. Choix des traitements:

Le manque de moyens sur place et surtout le manque de fonds nécessaires à l'entretien des canons traités après la fin de l'aide de l'UNESCO, nous ont incité, à la lumière des constatations faites sur place, à agir en deux temps:

- un traitement habituel de surface
- une protection par couplage galvanique.

2.1. Traitement des surfaces:

Les pièces ont d'abord été débarrassées des lichens, mousses et produits de corrosion de surface à l'aide de moyens mécaniques. Ensuite, le métal a été traité avec une solution à 15% d'acide phosphorique dans l'eau puis rincé, une neutralisation à l'hydroxyde de sodium à 10% dans l'eau a été faite suivie également de rinçages. Enfin, une solution à 5% de tannin à l'eau a été passée sur les canons en trois couches successives. Cette dernière technique a pour objectif de transformer les couches d'oxyde subsistantes en tannates moins réactifs.

Pour finir, l'ensemble a été recouvert d'une fine couche d'huile destinée à protéger le métal contre les chutes d'eau et le brouillard. Cette protection devra faire l'objet de renouvellements constants dès que les agents atmosphériques l'auront rendue moins efficace.

2.2. Protection par couplage galvanique:

Nous avons décidé de reproduire les phénomènes constatés mais en faisant le cheminement inverse. Nous avons disposé des plaques de zinc partout où il y avait un risque d'accumulation d'humidité ou d'eau, c'est-à-dire dans les lumières, sous les tourillons et dans les tubes des canons pour créer une protection par couplage galvanique (6). Bien entendu, cette protection a été mise en place avant le dépôt d'huile sur les surfaces des canons.

Nous avons choisi du zinc pur (type 99,995%) parce que les essais conduits sur la protection cathodique (7) montrent que les rendements faradiques sont de l'ordre de 90 à 95% (bien que le potentiel standard par rapport à l'électrode d'hydrogène soit moins bas pour le zinc que pour le magnésium ou l'aluminium) et que, même lorsque, par oxydation, ces rendements baissent, ils restent dans la zone où le fer est protégé (figure 1).

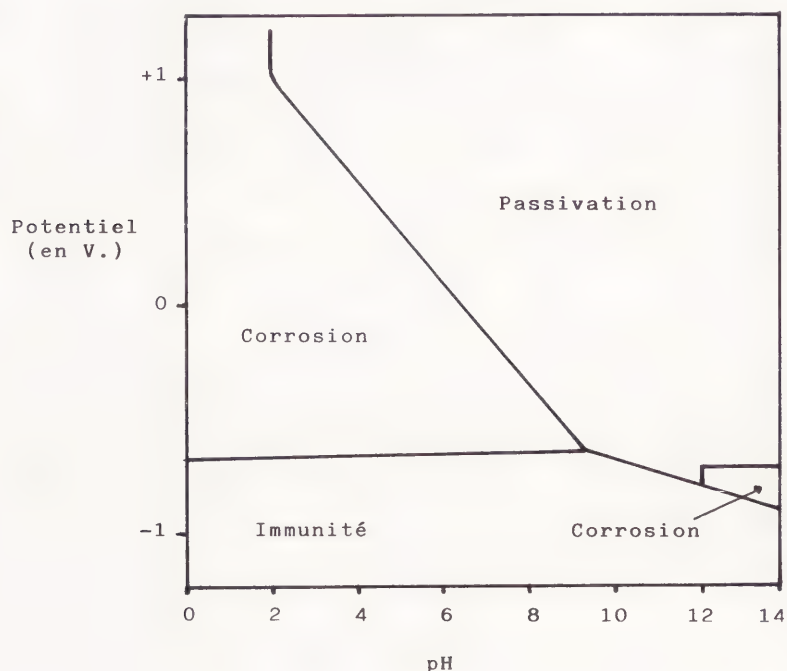


Fig. 1. Conditions d'immunité du fer en fonction du pH et du potentiel (d'après Pourbaix cité par Shreir)

Conclusion

Nous pensons que les techniques de protection par couplage galvanique, si elles sont appliquées dans des conditions particulières d'humidité relative, peuvent améliorer les conditions de conservation à long terme des gros objets métalliques. Il conviendra toutefois de vérifier sur le moyen et le long terme quels sont les résultats effectifs sur le terrain. Pour cela, les canons de la Citadelle Laferrière à Haïti devraient fournir une réponse aux questions que nous devons nous poser vis-à-vis de cette technique.

NOTES

1. J. GALLAND, Méthodes électriques de protection contre la corrosion, Corrosion et protection des métaux, CNRS, Paris, 1982, p. 263-265.
2. M.J. PRYOR, Bimetallic corrosion, Corrosion, 2nd edition, Butterworths, Singapore, 1971, 1-192, 1-211.
3. Bimetallic corrosion, Guides to practice in corrosion control, 14, Department of Industry in association with the Institution of Corrosion Sciences and Technology, Londres, 1979.
4. Cathodic Protection, Guides to practice in corrosion control, 9, Department of Industry in association with the Institution of Corrosion Sciences and Technology, Londres, 1979.
5. Note documentaire sur la protection cathodique, CEFRACOR, Paris, 1978.
6. J.B. COTTON, Appendix: Bimetallic corrosion, Degree of corrosion at bimetallic contacts, Corrosion, Butterworths, Singapore, 1979, 1-215, 1-217.
7. B. RACLOT, Les anodes de protection cathodique en milieu marin, choix et efficacité, Corrosion marine, moyens de protection, Actes du colloque de La Baulle, CEFRACOR, 1974, p. 273-278.

ABSTRACT

Outdoor sculptures of bronze erected the last decades are already heavily corroded due to the environment and due to the lack of maintenance. The so called patina is a corrosion product in the form of a porous layer of mineralic particles. These mineralic patinas may be preserved by the same techniques used for conservation of natural stones. A preservation process may consist of the following steps. Rinsing with water (mild detergents); (partial) removal of patina with packs of Na-hexametaphosphate; fixation (colour modification) of the patina with packs of K-Fe-cyanide; hydrophobation and strengthening of the patina by concentrates of (mono-molecular) alkylalkoxisilanes (eventually pigmented - graphite); application of a "sacrificing" layer of waxes.

KEYWORDS

Bronzes, sculptures, cleaning, preservation, conservation, packs, Na-hexametaphosphate, K-Fe-cyanide, alkylalkoxisilanes, waxes.



Fig 1 Milles 1936 ORPHEUS

AN ALTERNATIVE PRESERVATION METHOD FOR CORRODED OUTDOOR BRONZES

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1. Environment and the corrosion of bronze

In Stockholm and its immediate vicinity, there are a few hundred outdoor bronzes of all ages, the oldest Swedish ones about 200 years old - they have practically never been maintained; because of the aggressive urban environment, bronzes put up a few decades ago are already heavily corroded.

Most of these outdoor sculptures have been erected this century (and in principle been moulded in an identical composition for the alloy).

This gives an opportunity to study the development of patinas on bronzes.

The visual stages of bronze corrosion are as follows:

- original bronze surface or a "synthetical artistic" patina layer
- black "climatic" patina layer
- green strips and spots in the black patina, adjacent to areas of condensation and drainage. Snow prolongs the life of dry deposits of aggressive substances, and locally extends and enhances their corrosive effect
- green "climatic" patina layer with dirty relicts of black patina and yellow excrement discolorations
- a dirty grey-green patina.

Patina has a mineral composition, and in Stockholm it mostly consists of sulphates.

2. Preservation and bronze corrosion

In a modern urban environment, outdoor bronze corrodes relatively quickly. It loses its original appearance - bronze sheen or synthetic/artistic patina - as early as after 10-15 years - and turns black. A large proportion of the semi-antique bronze statues in public in Stockholm are mostly black or black with grey-green corrosion products; none of these sculptures - almost all of them not maintained - has retained its original patina. (Fig 1, Table I col 1-4).

	STATE				TREATMENT				
	1	2	3	4	5	6	7	8	9
Eldh 1913 VIKTOR BALCK			•			•	•	4	
Liljefors 1930 PLAY				•				5	
Jönsson 1935 GUSTAV V		•				•	•	4	•
Eldh 1937 ON THE FINISH LINE			•					9	
Fagerberg 1937 RELAY RACER			•			•		8	
Fagerberg 1937 SHOT PUTTER		•					•	10	
Strandman 1939 PER HENRIK LING		•				•		7	
Linde 1972 GUSTAV VI	•				•				•

col 8: number of treatments

Tab I State and treatment of nonmaintained bronzes examples, Olympic stadium 1912, Stockholm, Sweden

Most of the outdoor bronzes of similar age - as in a private collection - which have been preserved in a simple way (washing with water every autumn) still have, with a few exceptions, their original patina (or at least rests of it). They have fewer corroded areas on their surfaces. Owing to the absence of dirt deposits, no distinct runoff patterns have formed on their surfaces. (Fig 2 Table II col 1-4.)



Fig 2 Hjort 1946 MARGIT

col 8: number of treaments

Bronze surface artistic/synthetic patina	Climatic patina black	Climatic patina black/green	Climatic patina green	Rinsing with water + Na-hexametaphosphate	Cleaning with packs Na-hexametaphosphate	Fixation/colour modification with packs K3Fe(CN)6	Impregnation / "waxing" alkylalkoxisilanes	Final polishing graphite wax
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	STATE	TREATMENT							
	1	2	3	4	5	6	7	8	9
Maillol 1937 POMONE	●				●			2	
Maillol 1944 HARMONIE	●				●			3	
Maillol 1900 JEUNE FILLE AGENOUILLEE				●		●	●	5	●
Marini 1951 GRANDE CAVALLIO		●				●		5	
Rodin 1910 LENFANT PRODIGUE				●		●		7	
Laurens 1934 LES ONDINES (lead)		●						6	●
Gilioli 1958 LE CLOCHER	●				●			2	●
Duchamp-villon 1912 MAGGY	●				●			3	
Baskin 1971 MOURNING WOMAN	●				●			2	
Baskin 1973 ISAAC	●				●			2	
Baskin 1975 THE LOST SON	●				●			1	
Copy POSEIDON FROM ARTEMISION	●				●			2	
Vigeland 1915 PLAYING BEAR			●		●			6	
Hjort 1946 MARGIT		●			●			5	
Johnson 1932 WOMEN BY THE SEA			●			●		6	
Möllerberg 1926 THE BOXER	●				●			2	
Jönsson 1917 BOY WITH APPLE		●			●			4	●
Knöppel 1948 DEER	●				●			4	

Tab II State and treatment of maintained bronzes
examples, Marabou sculpture park, Sundbyberg, Sweden

It would appear obvious that continuous and simple treatment of bronze sculptures retards their aesthetic decay.

3. Strategies for the preservation of corroded bronze sculptures

3.1 General

The choice of strategies for preservation of corroded outdoor bronzes depends on historical/ethical considerations based on technical preconditions and is in most cases restricted by economical frames.

From an aesthetic point of view the result of a preservation activity should be some balance between the "colour" and the modelling of a sculpture.

3.2 "Reinstatement" of visual/optical aesthetic qualities

The following stages can be set down for this strategy:

- blasting of the climatic patina - the original synthetic artistic patina layer, if any, will have disappeared a long time ago
- application of a new patina layer on the bronze, preferably using the technique which the artist had applied. In most cases there is no knowledge of the original patination process, only hypotheses
- waxing which should be repeated every other year.

This necessitates removal and re-erection of the sculpture.

3.3 Retention of historic material, documentation of a historic process

This strategy endeavours to preserve the state of statues by using (modern) methods based on tested techniques. It comprises cleaning and if necessary removing/retouching of heavily corroded/environmentally affected areas, and protective measures to prevent further corrosion as impregnation of a porous patina (hydrophobation) and eventually a protective coating (lacquers, waxes) which may be pigmented (for example graphite).



Fig 3:1 State 1987

Fig 3:2 Treatment with packs 1988
foils against evaporation

Fig 3:3 State 1989

Fig 3 Preservation of bronzes
Eldh 1937
ON THE FINISH LINE

An alternative method applied for this strategy is described briefly in Chapter 4. Examples of the way in which the method can be used on heavily corroded and on maintained sculptures are given in Chapter 5.

4. An alternative for the preservation of outdoor bronzes

Whether it is synthetic or of climatic origin, patina has a porous formation of almost exclusively mineral materials (unless it is an oil patina). Mineral materials can be cleaned/removed, fixed/modified and made hydrophobic by well tested methods known from conservation of natural stone.

- The alternative preservation process may consist of the following steps:
- rinsing with ordinary water containing mild detergents (which absolutely have to be removed before an eventual hydrophobization);
 - cleaning (or eventual partial or total removing of patina layers), by a poultice of sodium hexametaphosphate solution and clay, contact time some hours (foilprotected);
 - fixing /colour modification of the patina by poultices of K-Fe cyanide solution and clay (foilprotected);
 - hydrophobic treatment by concentrates of alkyltrialkoxysilanes (in several treatment stages if necessary) with catalysts of metallic acid esters (e.g. 0.5 % titanium acid ester). Fig 3.

This treatment can be applied on cold and moist surfaces.

As a finish conventional waxing techniques can be used.

Silanes and waxes may be pigmented (for instance with graphite).

The appearance of the bronze after treatment is the same as that of a regularly waxed surface. Fig 3. Treatment can be carried out in situ, without major safety measures and without the need for large pieces of mechanical equipment. (Tables I and II, col 5-9.)

Reversibility: A coating of polymerized siloxanes may be removed by the application of packs of monomeric alkylalkoxysilanes in silica or clay protected against evaporation by Al-foils.

5. Results

Using this working strategy, some 50 outdoor bronzes, both maintained and nonmaintained ones, have been preserved in the last few years. Fig 4 ("in public"), Fig 5 and 6 (sculpture park).

There has been no deterioration so far (max 4 years) in the effect of the treatment.

6. Conclusions

If the object of bronze preservation is to retain historic patina to the greatest possible extent within restricted economical boundaries, a patina treatment comprising "silane waxing"/reinforcement, preceded by cleaning with Na-hexametaphosphate and fixation (if necessary with retouching) using K-Fe cyanide, can be applied.

Silanes and an eventual finish of ordinary waxes could be pigmented (graphite).

7. Acknowledgement

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8. Reference

PUEHRINGER, J, JOHNSON, B, Performance of utility bronzes in public - from information processing to a variant of preservation strategy, WIENER BERICHTE UEBER DIE NATURWISSENSCHAFT IN DER KUNST 1987/88 H4/5 (Editors: Vendl, Fichler, Weber, Banik), pp 64-160.

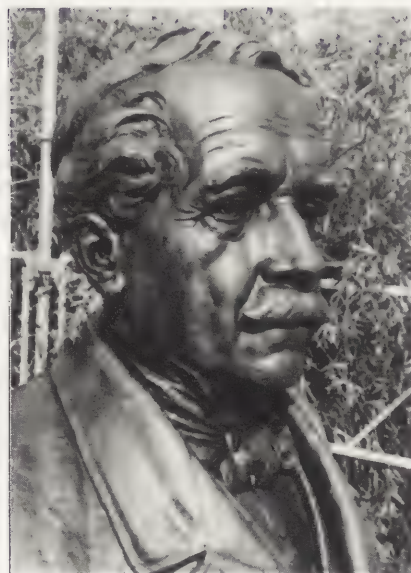
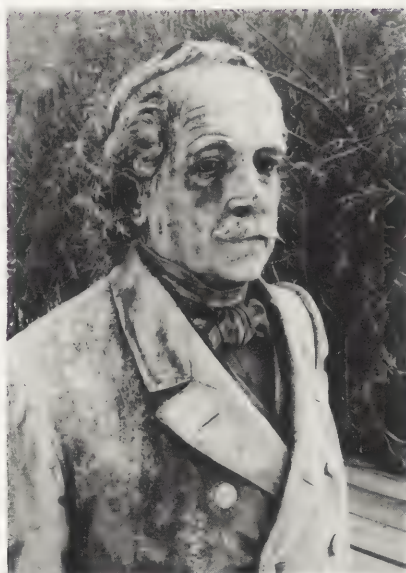


Fig 4:1 Börjeson 1893 NILS ERICSON

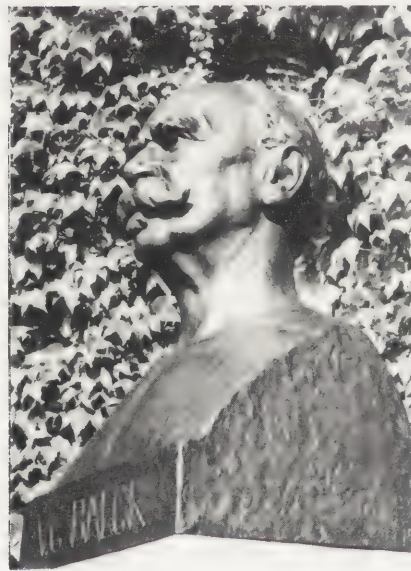
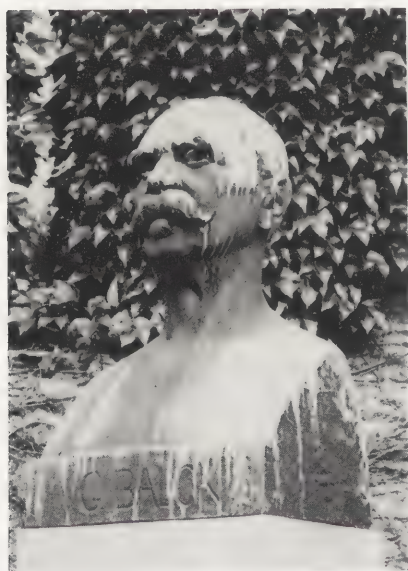


Fig 4:2 Eldh 1913 VIKTOR BALCK

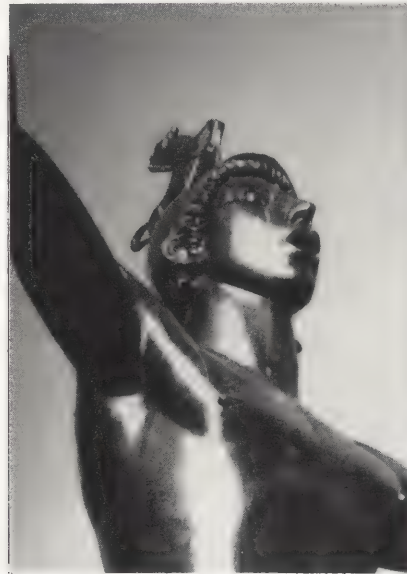


Fig 4:3 Milles 1926 SONG TO THE SUN

Fig 4 State and result of treatment, nonmaintained bronzes
"in public", Stockholm, Sweden



Fig 5:1 Marini 1951 GRANDE CAVALLLO



Fig 5:2 Maillol 1900 JEUNE FILLE AGENOUILLÉE



Fig 5:3 Rodin 1910 L'ENFANT PRODIGE

Fig 5 State and result of treatment, maintained bronzes
Marabou sculpture park, Sundbyberg, Sweden



Fig 6:1 Hjordt 1946 MARGIT

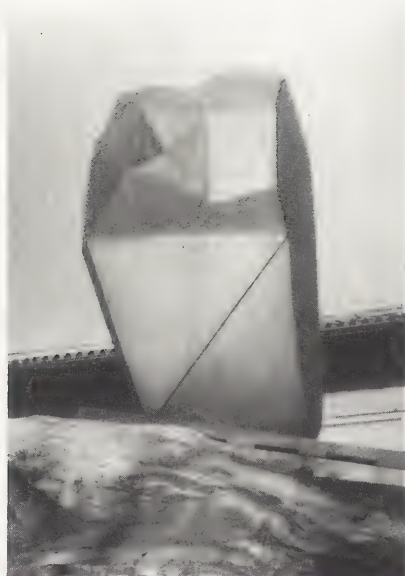


Fig 6:2 Gilioli 1958 LE CLOCHER



Fig 6:3 Jönsson 1917 BOY WITH APPLE



Fig 6 State and result of treatment, maintained bronzes
Marabou sculpture park, Sundbyberg, Sweden

RESUME

Le présent rapport offre les résultats d'une recherche intégrale qu'on a effectuée sur le monument à Minine et Pojarski planté sur la place Rouge à Moscou. Le monument fut réalisé par le sculpteur I.P. Martos de 1804 à 1818. Les études ont concerné l'état de conservation du groupe sculptural, du piédestal, des fondations et de la base du monument. On a, pour la première fois, obtenu les données sur la composition chimique et la structure de l'alliage de cuivre utilisé pour la coulée du groupe sculptural et des bas-reliefs. Sont étudiées les propriétés de fonderie, physico-mécaniques et corrosives de cet alliage et déterminées la composition des phases et la structure des superpositions superficielles. On a défini les grandes options pour les travaux de restauration à effectuer.

MOTS-CLEFS

Alliage de cuivre, superposition, composition, structure, corrosion, sculpture monumentale.

ETUDES COMPLEXES DU MONUMENT A MININE ET POJARSKI

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Introduction

Le monument à Minine et Pojarski fut érigé en 1818 sur la place Rouge à Moscou et représente une oeuvre d'art plastique remarquable. Ce fut le premier monument de l'ancienne capitale qui perpétua l'exploit du peuple russe. Créé par les artistes russes - sculpteur I.P. Martos, métallurgiste V.P. Ekimov, architecte A.I. Melnikov et maçon K.S. Soukhanov - il témoigne que la Russie de l'époque du classicisme fit naître des artistes doués et ayant possédés une grande maestria dans la fonderie d'art et dans l'art plastique.

Les collaborateurs du VNIIR conjointement avec les scientifiques d'autres centres de recherche ont, pour la première fois, fait des études intégrales qui concernaient non seulement l'étude du groupe sculptural et des bas-reliefs, mais aussi les inscriptions, le piédestal, le perré, les fondations et la base.

L'examen des fonds de diverses archives de Moscou et de Léninegrad a permis de révéler et de collecter, d'une manière assez complète des renseignements circonstanciés sur l'histoire du monument, sur la participation à sa création d'éminents personnalités historiques, sur le choix de l'endroit de son érection à Moscou, sur son transfert et sur les travaux de restauration précédents.

L'examen en plein air de toutes les composantes du monument a permis de révéler les particularités de leur état. Le groupe sculptural comprend une figure de Pojarski assis sur le banc, une statue en pied de Minine, un casque avec deux oreillons, un glaive, un bouclier et une plinthe. On a ouvert la trappe d'une forme irrégulière se trouvant sur le banc derrière la figure de Pojarski ce qui a permis de pénétrer à l'intérieur de cette dernière et du piédestal. Le piédestal est aussi creux ce qui ne **contrarie pas les renseignements fournis par diverses archives et publications (1,2).**

La technologie de fabrication du groupe sculptural colossal à un seul coup d'après un modèle de cire coulé représente un intérêt particulier. La description du processus de fonderie du monument à Minine et Pojarski est fournie par divers matériaux d'archives et de publications périodiques de cette époque (3-5). La technologie de fonderie du groupe sculptural et des bas-reliefs du monument d'après un modèle coulé a assuré au maximum une haute homogénéité de la composition et de la structure de l'alliage et une haute qualité de la surface des moulages. Qui plus est, l'absence de joints entre les parties exclut l'inhomogénéité de surface et des contraintes intérieures. Il faut remarquer une bonne qualité de fonderie et de traitement de la surface extérieure. La qualité de cette dernière est conditionnée par le mâtage et le cannelurage qui ont assuré une haute densité et une texture lisse. Cependant à l'heure actuelle la texture cannelée de surface sculpturale d'auteur est perdue, ce qui est apparemment dû à des travaux de restauration peu qualifiés. Seules quelques petites portions gardent les restes insignifiants et fort lisses du cannelurage. Plusieurs portions de la surface de l'alliage offrent un réseau de rayures en désordre qui sont dues à l'utilisation de gros abrasifs lors des restaurations précédentes. Des insertions d'auteur de forme régulière (carrée, rectangulaire, ovale) avec le mâtage des bords sont détectées sur la surface extérieure des figures et sur la plinthe. Dans les parties supérieures des figures (sur les têtes et sur les épaules) on observe des défauts de fonderie.

L'enveloppe sculpturale présente beaucoup de défauts de nature différente: des fissures débouchantes et non débouchantes, des pores et des orifices de diverses formes et dimensions. Il y a plusieurs refectons effectuées en vue d'élimination de défauts de l'alliage lors des travaux de restauration: bouchons de plomb, brasures à l'étain et au plomb, mastics, enduits à base de résines, de peintures à l'huile, de bitume, de mortiers de béton, etc. Des défauts exerçant une influence négative sur la robustesse constructive du monument sont détectés dans les parties inférieures des pieds des deux personnages et sur le plan horizontal supérieur de la plinthe. La plinthe a beaucoup de diverses

fissures dont une partie forment des trous béants de grandes dimensions. La plupart de ces défauts sont causés par les éléments technologiques de fer.

On a mesuré l'épaisseur du moulage du groupe sculptural à travers les fissures débouchantes dans certains endroits accessibles. Dans la partie supérieure des figures elle est égale à 5-7 mm, l'épaisseur du banc est de 60 à 120 mm, celle du pan supérieur de la plinthe est égale à 25 mm, les pièces d'insertion d'auteur ont l'épaisseur de 5 mm et les pans latéraux de la plinthe sont de 40 à 50 mm d'épaisseur.

Les données relatives à la composition de l'alliage de cuivre, à partir duquel sont coulés le groupe sculptural et les bas-reliefs fournies par diverses publications et sources d'archives sont contradictoires. Tout d'abord toutes ces sources disent que le monument est coulé à partir du bronze. Dans les archives on indique la composition suivante de la charge utilisée pour la fonderie du groupe sculptural: cuivre de balonnette - 1000 pouds, (1 poud = 16,38kg), étain anglais - 10 pouds, zinc - 60 pouds (3,5). C'est à dire le moulage aurait dû contenir 93% de cuivre, le bronze. Par exemple, la publication (6) nous apprend que le bronze du monument à Minine et Pojarski comprend "des additions insuffisantes de zinc et de plomb".

C'est pourquoi l'étude physico-chimique de l'alliage a constitué une des orientations principales des investigations. La prise des échantillons de divers endroits de l'enveloppe sculpturale a été faite pour permettre l'étude de la composition chimique et de la structure de l'alliage. Pour apprécier la ségrégation majeure éventuelle (formation de l'inhomogénéité de la composition chimique dans divers endroits du moulage) on choisissait les échantillons sur divers horizons du moulage et dans diverses parties d'une figure (épaule, dos, bras, pied, banc, etc.). On a aussi étudié les échantillons d'alliage pris des bas-reliefs et du casque qui furent coulés à part. Les échantillons ont été essentiellement pris dans la cavité intérieure en forme de limaille, de copeaux de métal et de petits morceaux sciés.

Les résultats des analyses font l'objet du tableau représenté sur la page finale.

Le cuivre et le plomb sont déterminés par la méthode électrolytique gravimétrique; l'étain, le plomb, le fer, le nickel, par la méthode d'absorption atomique. Certains échantillons de l'alliage ont été étudiés à l'aide d'un micro-analyseur à balayage JSM-35 CF moyennant une sonde électronique (capacité d'analyse est de 2 à 3 μ).

Les différentes méthodes utilisées pour l'étude ont démontré une bonne reproductivité des résultats analytiques. On a déterminé que l'alliage utilisé pour la fonderie de la composition sculpturale, du casque et des pièces d'insertion d'auteur représente un laiton, alliage du cuivre avec le zinc dont la teneur en cuivre est en moyenne de 88 à 83%, en zinc, de 12 à 14%, en étain, de 0,6 à 0,8%, en plomb, de 0,2 à 0,4% y compris des additions insuffisantes de nickel, d'argent, de fer, etc. La teneur en étain dans les échantillons pris dans les bas-reliefs avant et arrière est un peu supérieure à celle indiquée plus haut et constitue 1,2 à 1,4%, celle en zinc est respectivement inférieure et constitue 8,8 à 10,9%.

L'alliage se présente homogène dans diverses sections ce qui témoigne de l'absence de ségrégation majeure aussi bien en hauteur du monument que dans les limites d'un seul horizon. Le laiton d'une telle composition a une petite valeur d'intervalle de cristallisation et doit posséder une haute coulabilité (capacité de remplir des formes compliquées y compris des canaux fins), une basse disposition pour la formation de cavités de moulage concentrées.

On a détecté très peu de pores dissipés dans les échantillons, le moulage est bien dense. La formation de cavités de moulage concentrées fut prévenue par un système de coulée bien réfléchi et réalisée.

L'étude de la structure de l'alliage de fonderie a été poursuivie dans les conditions de lumière ordinaire et polarisée au moyen des microscopes MM-9 (MM-9) et "Neophot-2" à divers agrandissements. On a aussi utilisé à cet effet le microscope-micro-analyseur électronique à balayage "JSM-35 CF".

Les résultats des recherches témoignent de la qualité identique de la microstructure de l'alliage dont les échantillons ont été pris dans divers endroits de la sculpture. La structure de tous les alliages étudiés est monophasée à base d'une solution -dure du zinc et de l'étain dans le cuivre ce qui s'accorde bien avec les diagrammes de l'état des systèmes Cu-Zn et Cu-Sn. On voit les dendrites de cette phase avec les traces de la ségrégation cristalline, qui se manifeste faiblement à l'attaque chimique ou est absolument absente (différence d'après la composition chimique à l'intérieur des cristaux d'une solution dure). On ne voit nettement les pores sur les bords des grains que sur des certaines sections polies métallographiques. Quant aux phases excessives, on ne les a pas décélées.

L'examen des sections polies métallographiques avec une sonde électronique n'a pas révélé de ségrégation cristalline substantielle de l'alliage. On a détecté quelques microproportions noires, riches en zinc, et claires, riches en étain, qui se sont formées à la suite de la ségrégation dendritique. Ainsi, on a découvert que la composition sculpturale du monument à Minine et Pojarski avait été coulée à partir du laiton, alliage de cuivre et de zinc, et non du bronze comme on le pensait avant. Selon la teneur en éléments d'addition et impuretés cet alliage est proche des alliages industriels contemporains Л 090-1, Л 085-1 (Л 090-1, Л 085-1) /GOST 15527-70/.

Les données fournies par diverses publications sur les propriétés de fonderie, physico-mécaniques et corrosives des alliages dans le système cuivre-zinc témoignent du fait que la variation desdites propriétés est fort influencée par des tiers additifs (7). Vu que l'alliage à partir duquel fut coulée la composition sculpturale du monument à Minine et Pojarski diffère un peu, quant à sa teneur en éléments d'addition et impuretés, des laitons industriels contemporains, nous nous sommes intéressés à étudier ses propriétés. Pour procéder à l'étude permettant de déterminer l'influence de l'étain, du plomb, du fer et du nickel sur la structure et les propriétés du laiton on a fabriqué des alliages où la teneur en ces éléments correspondait quantitativement aux données obtenues. La fusion a été réalisée dans un four à vide avec une pression excessive d'hélium pour diminuer l'oxydabilité des alliages et la perte au feu des éléments. La vitesse de refroidissement des alliages dans les matériaux étudiés a été constante et constituait 15 degrés/min. On introduisait tour à tour dans le cuivre en fusion du fer, du nickel, de l'étain, du zinc, du plomb. À l'aide de l'analyse thermique différentielle on a établi les principaux paramètres de l'alliage étudié: $T_{\text{liquidus}} = 1050^{\circ}\text{C}$, $T_{\text{solidus}} = 990^{\circ}\text{C}$, $T_{\text{cristal}} = 600^{\circ}\text{C}$, $t_{\text{crit.}} = 4 \text{ min.}$

Les études métallographiques des alliages d'essai ont démontré que l'introduction dans le laiton de l'étain, du plomb, du fer et du nickel exerce une certaine influence sur la structure. Ainsi, l'introduction d'un additif d'étain (jusqu'à 0,75%) conduit à l'apparition dans la solution α -dure Cu-Zn de la ségrégation dendritique et d'une faible porosité. L'introduction du plomb (jusqu'à 0,42%) diminue dans une certaine mesure la porosité et donne des inclusions rares et insignifiantes des sphéroïdes. Le fer en quantité jusqu'à 0,3% diminue la grandeur du grain. L'addition du nickel ne dépassant pas 0,2% n'exerce pratiquement aucune influence sur la structure de l'alliage.

À la suite des essais réalisés on a réussi à déterminer le retrait linéaire, la coulabilité et la dureté de l'alliage. Pour déterminer les paramètres des propriétés de fonderie on a effectué la fusion du métal dans un four à l'induction à creusets du type МСТ-006 (ICT-006) sous une couche de charbon de bois. La coulée du métal dans les moules d'essai se faisait à une température de 1150 à 1200°C. La coulabilité de l'alliage, déterminée par la coulée des échantillons spiraux, a constitué 54,3 cm. Le retrait linéaire de l'alliage, mesuré à l'aide de l'appareil de Bolchakov, a constitué 1,44%. La dureté de l'alliage d'essai est égale à 59,6 kg/mm².

À la suite des essais de corrosion réalisés dans les chambres imitant une atmosphère industrielle durant 360 jours à un régime de $\text{C}_{\text{SO}_2} = 5 \text{ mg/mm}^2$, $\text{H} = 95\%$, $\text{T} = 340^{\circ}\text{C}$ on a établi que la vitesse générale de corrosion des alliages constitue $0,46 \cdot 10^{-8} \text{ g/cm}^2 \cdot \text{jour}$. La corrosion des alliages se poursuit avec extinction dans le temps et avec formation de couches protectrices; elle a un caractère régulier.

La comparaison des résultats obtenus pour les alliages d'essai, analogues à l'alliage du monument, avec les caractéristiques des laitons industriels a démontré que leurs propriétés de fonderie

physico-mécaniques et technologiques sont proches. Cependant il y a quelques différences dans le comportement concernant la corrosion. On a constaté que le processus de corrosion des laitons Л-85 (Л-85) et Л-80 (Л-80) se poursuit d'une manière plus intense par comparaison au laiton Л 090-1 (Л 090-1) et aux alliages du monument. Ce fait doit être dominant lorsqu'on doit résoudre le problème relatif aux pièces d'insertion et à la réfection pendant les travaux de restauration, car c'est justement le comportement corrosif dans les conditions atmosphériques en plein air qui détermine la formation de la patine naturelle sur les alliages de cuivre.

On a aussi étudié le revêtement de protection et décoratif du groupe sculptural et des bas-reliefs. L'examen a démontré que sur leurs surfaces il y a un revêtement inhomogène quant à sa couleur et son épaisseur qui exerce une influence négative sur la perception de l'effet quasi relief du monument. On a détecté sur les portions protégées contre les effets néfastes de l'atmosphère un revêtement artificiel gris-noir (qui couvre moins de la moitié de la surface totale). Ledit revêtement a des indices manifestes de dégénération active en patine verte naturelle (taches, traces de fuite, inclusions fines et grosses etc.). Les portions découvertes de l'alliage (plus de moitié de toute la surface) ont une patine naturelle, dont la couleur varie du vert bleuâtre jusqu'au vert de malachite. On voit sur cette patine un revêtement artificiel transparent du brun jaunâtre qui représente apparemment une pellicule de vernis. On voit des traces de fuites dues à la corrosion sur quelques portions de la surface à proximité des orifices débouchant dans l'alliage et, aussi, dans les endroits de réfections de restauration. Certains endroits de réfection éliminant des défauts sont couverts d'une couche de peinture (couleur verte foncée, jaune, grise). Les décapages d'essai et l'étude de la composition des phases et de la structure des composantes minérales et organiques de stratification superficielle sur l'alliage du groupe sculptural et des bas-reliefs à l'aide des méthodes de phases aux rayons X, de chromatographie sur couches minces, de spectroscopie infrarouge ont démontré qu'elles étaient inhomogènes quant à leurs composition, épaisseur, couleur et texture. Outre le revêtement sulfo-organique combiné certaines portions ont une patine verte naturelle composée de sulfates basiques de cuivre et de brochantite et couverte, presque partout, d'une fine pellicule organique contenant dans sa composition du vernis glycérophtalique. Dans certains endroits, sous le revêtement artificiel noir il n'y a qu'une patine brune due à l'oxydation.

Les résultats des études visant à déterminer l'état de conservation du monument ont permis de formuler les grandes options des travaux de restauration à accomplir qui doivent comprendre: une amélioration de la robustesse de construction du groupe sculptural et des bas-reliefs, le rétablissement de la capacité portante de la plinthe, l'obturation de plusieurs défauts de l'alliage de fonderie, le décapage et le traitement de protection et décoratif de la surface du groupe sculptural et des bas-reliefs. Les études pétrographiques du granit à partir duquel est réalisé le piédestal, l'évaluation du degré de sa destruction et de l'état de conservation de sa surface posent encore un problème concernant la réalisation des travaux de restauration, à savoir, l'élimination des encrassements, le scellement des défauts et des joints, la prise des mesures nécessaires visant à assurer l'évacuation de l'humidité, due à la condensation, de la cavité intérieure dans un système de drainage souterrain. On se propose aussi d'arrêter les processus de destruction active pour garantir la conservation physique du monument, pour augmenter sa robustesse et sa résistance aux effets néfastes de l'environnement, ce qui, en effet, permettra de conserver l'expressivité artistique du monument en question.

BIBLIOGRAPHIE

1. Archives historiques centrales de l'URSS, f.733, inv.16,d.8, f 27, 1815.
2. Vinogradov N.D. Monuments architecturaux de Moscou /Gorodskoie khoziaistvo Moskv (Economie municipale de Moscou) M. 1947 № 6, p.32
3. Nouvelle historique sur la fonderie en bronze du monument au Citoyen Minine et au prince Pojarski /Vestnik Evropy/ (Messager de l'Europe) Spb., 1817. -№20. p.268-275
4. Monument à Minine et Pojarski /Syn Otetchestva/ (Fils de la Patrie). Spb., 1817. -№1. p. 175-188
5. Archives historiques centrales de l'URSS. f.1285, inv.8, d.411, f.163, 206-207, 1811

6. Odnoralov N.V. Sculpture et matériaux de sculpture. -M. Sovétski khoudijnik (Peintre soviétique), 1982. -P. 233
7. Smiriaguine A.P., Smiriaguina N.A., Belova A.V. Alliages et métaux non ferreux industriels. -M. Métallourguia (Métallurgie). -1974. P. 483.

Tableau

Résultats de l'étude des alliages de fonderie du monument à Minine et Pojarski
(pourcentage en poids)

Endroits de prise des échantillons	C u i v r e		E l e m e n t s d' a d d i t i o n						I m p u r e t e s	
			Z i n c		e t a i n		p l o m b		f e r	
	Chim.	El.	Chim.	El.	A	El.	Chim.	A	A	Chim.
Figure de Minine										
épaule	86,62	87,4	11,95			0,63	0,19			
bas de la chemise	84,4		13,76		0,76		0,63		0,15	0,08
piéd gauche	84,84	88,0	13,43	11,80	0,80	0,74	0,40	0,38	0,45	0,08
Figure de Pojarski										
dos du haut	85,48		12,64		0,75		0,28	0,26	0,77	0,08
dos au milieu	86,46		12,37		0,65		0,26	0,26	0,38	0,08
bras droit	85,10		13,26		0,83		0,42	0,32	0,28	0,01
insertion sur le bras	83,22		14,65		0,79		0,36	0,28	0,90	0,09
talon droit	85,50	86,0	13,44	13,30	0,70	0,27	0,24	0,28	0,32	0,10
Band										
haut arrière	84,60		14,22		0,70		0,28	0,26	0,34	0,08
haut milieu	87,14		11,01		0,72		0,23	0,20	0,80	0,10
haut avant	85,20		13,83		0,50		0,17	0,30	0,22	0,08
milieu avant	85,92		12,68		0,70		0,28	0,32	0,34	0,08
bas avant	84,62	85,0	14,01	14,60	0,80	0,38	0,31	0,33	0,12	0,08
casque	85,36	87,2	14,40	10,40	0,72		0,38	0,25	0,25	0,09
bas-relief avant	88,7		9,8		1,4		0,4		traces	trace
bas-relief arrière	86,8		10,9		1,2		0,4		traces	trace

Chim.-analyse chimique; A-analyse d'absorption atomique;

El.-analyse électronique par sonde

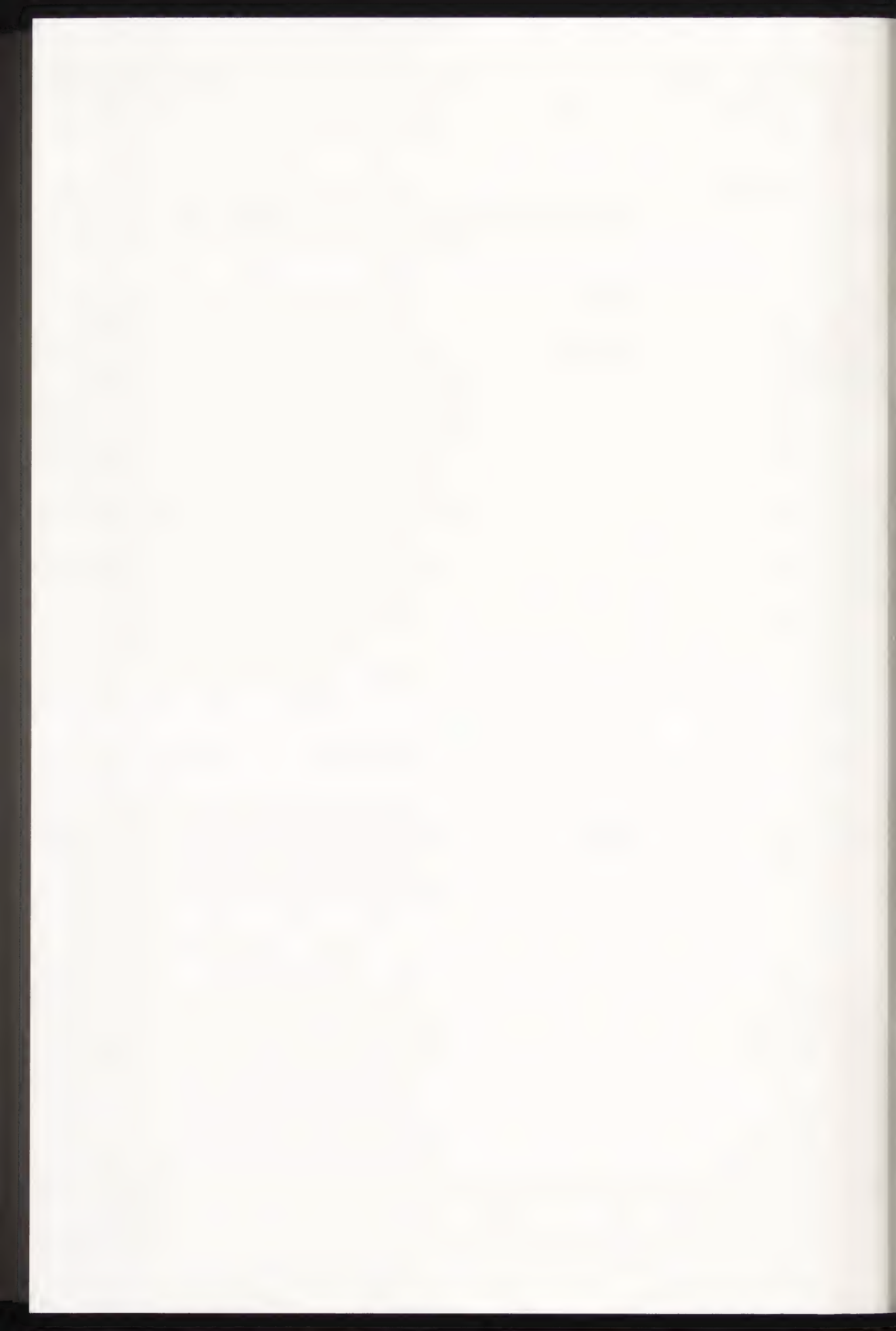




Working Group 23

Icons

Icônes



RESUME

Le rapport est écrit à l'occasion du millénaire du baptême de la Russie. Il expose brièvement l'histoire de la restauration des icônes à partir de la deuxième moitié du XIXe siècle jusqu'à nos jours; les principes et les méthodes de leur restauration dans les différentes périodes de l'histoire du pays, le rôle de l'enlèvement des repeints et des renouvellements, commencé activement après la révolution, ce qui nous a permis de retrouver et d'écrire une histoire objective de l'art russe ancien.

L'auteur examine en particulier l'état actuel des études, de la conservation et de la restauration des icônes, les problèmes de la recherche et de la mise en pratique des méthodes complexes contemporaines de leur restauration, les objectifs de l'étude et de la sauvegarde de la peinture d'icônes.

MOTS-CLES

Repeint, renouvellement, "Image pour prière", ouverture par couches, ajouts, méthode complexe, conservation, enlèvement des repeints et leur transposition sur un nouveau support.

LA RESTAURATION DES PEINTURES D'ICONES EN URSS

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La réparation, le renouvellement, la restauration des peintures d'icônes ont pris naissance avec l'apparition de l'icône. L'histoire nous a rapporté dans les documents et les monuments les noms de bon nombre d'icônes anciennes, médiévales et modernes, renouvelées par des peintres d'icônes renommés sur l'ordre des grands-ducs, des tzars, des patriarches.

Le but principal du renouvellement de l'icône presque tout au long de son existence (jusqu'à la deuxième moitié du XIXe siècle en Russie était l'aspiration de rendre à l'icône sa fonction principale d' "Image de prière", ce qui prédéterminait et maintenait en fin de compte les points de vue de vieille date sur l'essence même de la restauration.

Il est naturel que de siècle en siècle, les modifications de l'idéologie, la manière de voir le monde, particulièrement aux XVIIIe - XIXe siècles, conformément aux points de vue "les plus récents" de ce temps-là sur l'art orthodoxe dans l'esprit de l'éclectisme byzantin-académique, l'image iconographique changeait elle-même, mais les principes et les méthodes du renouvellement de l'icône restaient invariables.

La nécessité de l'approche scientifique à la restauration des peintures d'icônes en Russie est apparue au cours de la deuxième moitié du XIXe siècle. La cause en était le changement de l'attitude de la société envers les monuments historiques et culturels, l'activité accrue de différentes sociétés scientifiques, en premier lieu archéologiques, et les activités de collection, lorsqu'on a commencé à concevoir l'icône non seulement comme un objet du culte, mais comme une oeuvre d'art.

Néanmoins jusqu'au début du XXe siècle la restauration des peintures d'icônes en Russie continuait à porter, en général, le caractère des renouvellements. Quelques icônes particulièrement honorées étaient sous protection, mais même les images, comme "La Sainte Vierge de Vladimir" (XIIe siècle), la "Trinité" de A. Roublev (XVe siècle) et autres, avec le consentement et sur l'ordre de l'Eglise ont subi plusieurs réparations et renouvellements dans la technique et la technologie de la peinture ancienne, connues d'après les sources littéraires, les observations, les traditions qui passaient de génération en génération.

A la fin du XIXe - début du XXe siècle, avant la révolution russe de 1917, les savants renommés, les peintres, les collectionneurs, les restaurateurs proposaient et exigeaient l'institution des principes et des normes nouvelles de la restauration des monuments historiques, visant à leur ouverture (élimination des modifications antérieures), restitution et conservation inconditionnelle. En même temps, avec le procédé traditionnel et toujours pratiqué de renouvellement des icônes, on commençait à utiliser la méthode d'ouverture de la peinture d'auteur en la débarrassant des couches superposées. Le processus de la formation et du développement de la restauration argumentée scientifiquement des peintures d'icônes, comme d'ailleurs des peintures murales, s'est avéré long, compliqué et contradictoire.

Le brusque changement de l'attitude envers le patrimoine culturel en Russie est en rapport direct avec la Grande Révolution socialiste d'octobre 1917. Le pouvoir soviétique dès ses premiers pas s'est posé la tâche de transférer en biens publics toutes les valeurs de la culture et de l'art, créées par les hommes pendant les millénaires. Ce n'est pas par hasard que les premiers décrets du pouvoir soviétique signés par V.I. Lénine concernant les problèmes de la culture et de l'art avaient pour objectif une garantie inconditionnelle de sauvegarde du patrimoine culturel du pays.

En octobre 1917, aussitôt après la révolution, la République soviétique en la personne du Commissariat du peuple pour l'Instruction a pris à sa charge la cause de l'Inventaire, de la sauvegarde, de la restauration et de l'utilisation des monuments historiques et culturels. Un Collège de toute la Russie pour les affaires de musées et la sauvegarde des monuments d'art et d'antiquité a été constitué près ce Commissariat; à son tour, près ce Collège a été créée une Commission pour les affaires de restauration avec ses ateliers architecturaux et artistiques. A la tête de cette Commission était I.E. Grabar, savant éminent,

peintre, homme social, qui a fait beaucoup alors et par la suite pour la collection et la sauvegarde du patrimoine historico-culturel du pays. C'est le nom de I. Grabar qui nous vient à l'esprit le premier quand il s'agit de l'organisation et du développement de l'école soviétique scientifique de la restauration.

La tâche très compliquée de l'expropriation, des recherches, du sauvetage et de la restauration du patrimoine culturel dans les conditions de la guerre civile, de l'intervention, de la famine, de la ruine, a été confiée à l'intelligentsia ancienne et nouvelle, à l'administration locale, aux organisations sociales.

Pendant ces premières années, après l'institution de l'organisation centrale de restauration, on a créé des ateliers de restauration de profil mixte dans les centres de la culture ancienne de l'Etat russe comme Kiev, Novgorod, Yaroslavl, Vologda, Pskov. On a ouvert de nouveaux départements de restauration ou on a élargi ceux déjà existants près les musées les plus importants de l'Etat - l'Ermitage, la Galerie Tretiakov, le Musée Russe, le Musée des Beaux-Arts, le Musée-Réserve dans le monastère de la Trinité St. Serge à Zagorsk.

En 1924, vu l'augmentation du volume des travaux de restauration, la Commission de toute la Russie pour les affaires de restauration et les ateliers de restauration près cette Commission ont été réorganisés en Ateliers centraux d'Etat pour la restauration (CGRM). Ces Ateliers sont devenus le centre unique de restauration, de production et de science pour la sauvegarde (restauration, conservation, ouverture) des objets d'art, d'antiquité et de mode de vie, conformément aux principes scientifiques nouveaux et aux méthodes élaborées par ces ateliers. Désormais tous les travaux dans le centre et sur place ont été effectués sous la surveillance et le contrôle du CGRM.

Pendant ces années, à côté du travail pratique pour la recherche, l'inventaire, la conservation et la restauration des oeuvres d'art, on a publié des ouvrages scientifiques, des instructions, on a organisé des expositions par lesquelles la Commission de toute la Russie et ses ateliers rendait compte de ses activités. En 1929 la première grande exposition des oeuvres d'art russes anciennes a été envoyée à l'étranger. Cette exposition se composait en général des oeuvres ouvertes après la révolution. Elle a eu un grand intérêt historico-artistique et de restauration. Pour les années 1920 l'existence de ces ateliers avec des objectifs clairs et pratiques témoignait que la sauvegarde du patrimoine culturel en Russie, et un peu plus tard dans les autres républiques est devenue une affaire d'intérêt national, et la restauration elle-même s'est transformée en matière scientifique et appliquée.

Pendant les années 1920-1930 des milliers d'oeuvres d'art de la peinture russe ancienne ont été restaurées, y compris les oeuvres uniques, devenues la base de l'histoire de l'art russe. Presque toutes ces oeuvres avaient des couches superposées très anciennes, de vieilles additions, des renouvellements et étant très compliquées, exigeaient une maîtrise exceptionnelle pendant la restauration.

Les erreurs grossières, les répressions commises à la fin des années 20 et pendant les années 30 lors de la lutte acharnée contre la religion, quand tout un nombre d'objets d'art ayant un caractère religieux a été détruit, vendu ou renvoyé dans les fonds d'Etat, les Ateliers centraux d'Etat pour la restauration (CGRM) ont été liquidés et leurs fonctions transmises à la Galerie Tretiakov (GTG). Tout cela, cependant, n'a pas pu empêcher le développement successif de la restauration. Les principes et les méthodes de la restauration continuaient à se perfectionner, on publiait des ouvrages scientifiques avec la participation des sciences naturelles.

La méthode d'ouverture des icônes, adoptée dans les années 20, se modifiait elle aussi, en particulier la méthode de conservation des rénovations se rapportant à des époques différentes et se trouvant dans les endroits de pertes (fragments de repeints), qui détruisaient l'intégrité artistique de la composition, ainsi que les méthodes des additions et des mises sur ton. Un travail peu soigné avait lieu souvent pendant les ouvertures et les additions, ce que nous voyons bien aujourd'hui grâce aux méthodes nouvelles de l'étude des peintures. Cette circonstance est devenue la cause du "retour" de la restauration scientifique contemporaine vers certains objets d'art restaurés dans les années 20, y compris vers les oeuvres remarquables, comme, par exemple, "Boris et Gleb" (XIV^e siècle, GRM).

En 1944, pendant la Guerre, conformément à la décision du Conseil

des Commissaires du peuple on a créé les Ateliers centraux artistiques de restauration (GCHRM, actuellement VHNRC I. Grabar) pour l'enregistrement, la recherche et le sauvetage des oeuvres victimes des opérations militaires. En fait, c'était la reconstitution des CGRM, liquidés en 1934, mais sans son département architectural. La restauration de l'architecture et de ses intérieurs se formait isolément et vers les années 1960, son réseau est devenu très important; il couvrait toutes les républiques fédérées et les villes anciennes de l'Union Soviétique.

En 1958, à côté des ateliers de restauration républicains déjà existants comme le Centre de toute le Russie I.E. Grabar à Moscou, le centre ukrainien à Kiev, lithuanien à Vilnius et autres, on a créé le Laboratoire central de recherches scientifiques pour la conservation et la restauration des biens de musée (VCNILKR) du Ministère de la Culture de l'URSS, qui a reçu à partir de l'année 1979 le statut de l'Institut de recherches scientifiques pour la restauration du Ministère de la Culture de l'URSS (VNIIR). L'objectif principal de la nouvelle organisation est l'élaboration et la mise en application dans la pratique de restauration des méthodes scientifiquement argumentées de l'étude, de la conservation, de la restauration et de la sauvegarde des objets d'art.

Le système d'organisation pour la restauration des fonds de musée du pays, existant aujourd'hui en URSS, y compris la peinture d'icônes, peut être considéré comme satisfaisant. Nous avons un Institut de tête, les ateliers républicains, les départements de restauration près les grands musées. Comme défaut principal de ce système il faut reconnaître la pénurie des cadres de restauration, le mauvais approvisionnement des ateliers en équipements, appareils et matériaux, le niveau insuffisant des salaires. Nous espérons résoudre ces problèmes du moins partiellement à l'aide des organisations sociales et du gouvernement dans les années les plus proches.

300 peintres-restaurateurs attestés travaillent aujourd'hui dans le domaine de la peinture en détrempe et trois fois plus de non-attestés qui doivent passer cet examen. Les cadres de restaurateurs se trouvent essentiellement dans les centres - Moscou, Léninegrad, dans les capitales des républiques fédérées, dans les villes russes anciennes - centres anciens de la culture orthodoxe. L'Institut de recherches scientifiques pour la restauration dispose de 20 restaurateurs travaillant avec des icônes; dans le centre I.E. Grabar il y en a 30, dans l'Association architecturale de restauration, 26, dans les Musées du Kremlin de Moscou, 6, dans le Musée Historique, 7, dans le monastère Danilovsky, 6, dans le Musée Russe de Léninegrad, 8, dans la ville de Istra, 7, de Yaroslavl, 17, de Kiev, 8, de Lvov, 24, de Minsk, 7, de Riga, 4, de Tallin, 4, et ainsi de suite.

Malheureusement dans la plupart des villes anciennes comme Novgorod, Pskov, Arkhangelsk, Kirillov, Riazan, Rybinsk, Rostov-Yaroslavsky, Ouglitch, Perme, Irkoutsk et autres, ayant de grandes collections de peintures russes anciennes, il n'y a qu'un ou deux restaurateurs. Leurs laboratoires ne sont pas convenablement équipés, ils n'ont pas de chimistes, physiciens, biologistes, ils se trouvent loin l'un de l'autre et loin du centre, le contrôle de leurs activités est difficile et souvent ils sont abandonnés à eux-mêmes, ce qui, naturellement, diminue la qualité de leurs travaux. Nous parlons et écrivons beaucoup du devenir et du développement de l'école scientifique de la restauration en URSS dans les décennies précédant les années 1960, et c'est juste. Cependant il faut reconnaître objectivement que la mise en application de la science dans la pratique avait alors plutôt un caractère épisodique. Les savants en sciences naturelles en règle générale, ne faisaient pas partie du personnel des ateliers. Le développement actif et la mise en application de la science dans la pratique commencent à partir du milieu des années 1950 avec l'arrivée des spécialistes en sciences naturelles, des historiens d'art, des archéologues dans les ateliers, les laboratoires et les instituts, avec la formation de départements pour la recherche scientifique, comme c'était au VNIIR, VHNRC I. Grabar, l'Ermitage, appelés à desservir l'art de la restauration, et finalement avec une conception nouvelle de l'attitude de la société envers le patrimoine culturel.

Parmi le grand nombre de problèmes qui se posent aujourd'hui devant nos restaurateurs, je voudrais mettre en relief quelques-uns des plus importants. Tout d'abord c'est l'aspiration à la mise en application et au développement des possibilités de la méthode complexe de l'étude et de la restauration des oeuvres d'art, et avant tout, des peintures d'icônes; deuxièmement, c'est

l'élaboration et l'application dans la science et la pratique de la restauration du contrôle sur la qualité d'exécution des travaux de restauration avant leur étape finale; ensuite, c'est la conservation des peintures d'icônes pour leurs préservation et restauration postérieure; et, finalement, c'est la formation des spécialistes de haute qualification, responsables du patrimoine culturel, de l'attitude critique envers les matériaux utilisés dans la pratique de la restauration.

La méthode complexe comprend l'étude, la restauration, les principes d'exposition d'un monument ou d'un ensemble par un groupe de spécialistes: historiens d'art, restaurateurs, chimistes, physiciens, biologistes, climatologues unis par le seul objectif - faire renaître le monument à la vie active avec une information complète et exhaustive sur ce monument (historique, technico-technologique, de restauration, de critique d'art, de conservation). Sans doute, ce travail ne peut être accompli que par de grandes collectivités de restaurateurs, de savants et de travailleurs de musée, munis d'un équipement moderne. En URSS ce travail peut être fait par quelques organisations seulement, car les petites unités de restauration, surtout périphériques, en leur grande majorité ne peuvent pas s'acquitter de cette tâche malgré leurs appels aux instituts locaux de profil différent.

La méthode complexe de l'étude et de la restauration, proposée par VNIIR, a été mise en pratique pour la première fois sur l'iconostase (60 icônes) de la Cathédrale de la Dormition du Musée-Réserve de Kirillo-Biélozersk. La même méthode a été appliquée lors du traitement des icônes très bien connues - "Le Saint-Signe" (icône bilatérale, XIIe siècle), "La Dormition" de Dionysos de la ville de Vologda, des sculptures polychromes du retable (XVe siècle) de Tallinn et autres. Ces travaux ont été accomplis sous la direction de Mme Olga Lélékova, docteur honoraire, Chef de Département des méthodes de restauration des peintures de dérempe de VNIIR. Les résultats des études et de la restauration ont dépassé toutes nos espérances. Tout un nombre d'ouvrages scientifiques a été publié basés sur ces résultats. Parmi eux, par exemple, l'étude de la couche picturale des icônes russes, la méthode du détachement et de la transposition sur de nouveaux supports des couches superposées de la peinture, les pellicules de protection et les colles nouvelles, les principes et le caractère de la documentation scientifique de restauration, la confection de la construction détachable des revêtements métalliques, le tirage des copies, l'attribution des oeuvres, et, finalement, l'ouvrage substantiel de Mme O. Lélékova traitant des résultats des recherches scientifiques de restauration obtenus sur l'iconostase de la Cathédrale de la Dormition du Musée-Réserve de Kirillo-Biélozersk et deux recueils de Phérapont, consacrés aux fresques de Dionysos et aux icônes, dont un des auteurs est Dr. G. Vzdrnov. La méthode complexe donne la possibilité de construire une théorie scientifiquement argumentée de la restauration des monuments de l'histoire et de la culture, contribue au relèvement de la qualité de la restauration; elle devient une bonne école pour de nombreux spécialistes du pays.

Le contrôle de la qualité du processus des travaux de restauration, et particulièrement lors de l'ouverture du monument, est basé sur l'application des méthodes physico-optiques, sur la documentation photographique avec un examen du processus des travaux pendant les réunions du Conseil de restauration. On a adopté la méthode de l'ouverture des monuments compliqués avec l'utilisation obligatoire des microscopes. Nous voudrions également, à côté des méthodes simples, utiliser les ordinateurs pour le contrôle de la qualité, pour l'expertise de l'état d'intégrité.

La conservation du monument est considérée comme une mesure principale et la plus urgente de son sauvetage. Nous en parlons et écrivons beaucoup étant donné que tout un nombre de monuments dans les fonds de musée, les collections privées, se trouvent en mauvais état (écaillés, détériorations biologiques) et exigent l'exécution de travaux de conservation. Ces travaux ne sont pas très prestigieux pour les restaurateurs et, de ce fait, malheureusement, leur volume laisse à désirer.

Ces derniers temps, on se prononce avec insistance contre l'utilisation des matériaux chimiques nouveaux (polymères) dans la pratique de la restauration et pour le retour vers les matériaux traditionnels, éprouvés par les siècles. Il faut prendre en considération cette opinion. Nous utilisons les nouvelles substances polymères depuis plusieurs décennies (30-40 ans) et elles n'ont pas encore subi l'épreuve du temps assez longtemps pour s'en faire une idée. Il faudrait alors continuer les études sous tous les aspects des matériaux nouveaux, sur leur "survivance" et leur compatibilité avec les monuments de la culture. Il faudrait

faire de même avec les matériaux traditionnels.

Une importance particulière revêt aujourd'hui le problème du choix, de la formation, de l'attestation des cadres de restaurateurs. La pratique et la théorie de la restauration des oeuvres d'art sont devenues aujourd'hui trop compliquées. Elles ne peuvent pas être comparées avec la théorie et la pratique des années 50-60, sans parler de la période des années 20-30, quand dominait la méthode individuelle de l'apprentissage et de la profession de restaurateur.

De nos jours le problème de la préservation du monument, l'attitude particulière envers les oeuvres d'art, exigent du restaurateur non seulement une connaissance des processus de la restauration elle-même, mais outre cela, une large érudition dans le domaine de l'histoire de l'art, de l'application pratique des méthodes des sciences naturelles, des méthodes de stockage, etc. Quel que soit le contrôle sur l'intégrité et la restauration des oeuvres d'art, il serait peu efficace sans spécialistes, érudits professionnels, dévoués à leur tâche.

Conclusion

L'école russe soviétique de la restauration, et en particulier celle des peintures d'icônes, a passé une voie longue et compliquée de son développement, à partir de la mise à jour des questions pressantes jusqu'à la résolution pratique scientifiquement argumentée des problèmes et des objectifs de restauration, assurant la régénération et l'intégrité du patrimoine culturel inappréciable du pays, qui représente une partie du patrimoine culturel mondial. Cette voie n'est pas encore terminée, c'est la logique même du développement de chaque grande entreprise. Notre tâche d'aujourd'hui consiste à multiplier nos efforts dans la lutte pour la sauvegarde du patrimoine, créé par les peuples du monde au cours des millénaires.

Le déchiffrement des abréviations

- 1) AN de l'URSS - Académie des Beaux-Arts de l'URSS.
- 2) VCNILKR - Laboratoire central scientifique de l'URSS pour la restauration et la conservation des biens d'art de musée (1958-1978) du Ministère de la culture de l'URSS.
- 3) VNIIR - Institut de recherches scientifiques de l'URSS pour la restauration (réorganisé du VCNILKR au VNIIR en 1979) du Ministère de la culture de l'URSS.
- 4) VHNRC I. Grabar - Centre artistique de toute la Russie pour la restauration scientifique I. Grabar (ancien GCHRM) Moscou.
- 5) GCHRM - Ateliers centraux artistiques de l'Etat pour la restauration.
- 6) GTG - Galerie Tretyakov (Moscou).
- 7) GRM - Musée Russe (Léningrad).
- 8) GMMK - Musées du Kremlin de Moscou.
- 9) GE - Ermitage (Léningrad).
- 10) GIM - Musée Historique (Moscou).
- 11) CGRM - Ateliers centraux de restauration (1924-1934, Moscou).
- 12) Les ateliers de restauration dans les villes de l'Union Soviétique mentionnés dans le texte, exercent leurs activités auprès des musées de ces villes, ou bien les auspices des Ateliers spéciaux de restauration scientifique, des Centres de restauration ou des Administrations pour la protection des monuments.

RESUME

Au courant depuis plusieurs années des travaux de restaurateurs de musées, organisations de restauration scientifique et commerciale et tenant compte de l'expérience acquise à l'Institut de recherche pour la restauration, sur divers matériaux d'archives et publications, on offre une analyse de la période initiale et de l'état actuel de la restauration des icônes en URSS. Une attention particulière est portée à la méthode élaborée au VNIIR.

MOTS-CLES

Ikône, repeint, décapage, rénovation, endommagement, facture, microscope, restauration commercialisée, restauration scientifique.

PROBLEMES DE RESTAURATION DES ICONES RUSSES

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Introduction

Les procédés de travail dans le domaine de la restauration des icônes sont beaucoup plus stables que ceux des autres arts. Cependant les questions relatives à ce sujet sont actuellement arrivées à maturité et il y a lieu de les discuter. On considère comme critique la période présente dans le développement de la restauration des icônes. Il existe à la fois deux modèles du processus de restauration. Un modèle est moins répandu, mais permet de réaliser les travaux de restauration à haut niveau. Quant à l'autre modèle, il est largement répandu, mais la qualité des travaux laisse à désirer.

Problèmes de restauration des icônes russes

Les pays où la peinture d'icônes est née comme un objet de culte disposent aussi de plus importantes collections d'icônes dans leurs musées. Parmi ces dernières la part des icônes russes est assez considérable.

Les monuments de divers pays réunis sous le nom commun d'"icône" diffèrent quant à leurs caractéristiques stylistiques et technologiques comme diffèrent les méthodes de leur étude et de leur restauration. Je veux m'attarder sur quelques détails des problèmes relatifs à l'étude et la restauration des icônes en Russie. L'histoire de l'icône russe a connu pas mal de moments durs, même dramatiques. L'icône russe a une particularité technologique très singulière: il s'agit de l'emploi de l'huile de lin cuite qu'on appliquait sur la surface picturale en vue de sa protection. L'inconvénient de ce procédé consiste en ce que, avec le temps, l'huile devenait très sombre et il fallait repeindre les images. L'organisation du travail dans le domaine de la peinture d'icônes était telle que tous les maîtres de qualification médiocre, qui n'étaient pas à même de créer de nouvelles icônes, avaient recours à cette pratique. En exécutant les rénovations on n'annulait jamais les images anciennes (on ne le faisait qu'en cas d'exception), on les recouvrait d'une nouvelle couche picturale. Il y a des icônes ayant jusqu'à 10 couches superposées, même plus, les rénovations étaient faites intégralement ou partiellement. Cette façon d'agir s'est révélée d'une part, favorable à l'état de conservation des icônes: des couches épaisses superposées étaient bien solides et protégeaient, dans des cathédrales non chauffées, les anciennes couches picturales originelles contre les effets nuisibles dus aux variations de température et d'humidité en hiver, au printemps et en automne. Mais d'autre part, cette écorce multicouche rend son enlèvement extrêmement difficile pour le restaurateur. Pis, son enlèvement présente beaucoup de danger pour la couche picturale originelle. Les icônes sont considérées en URSS parmi les objets fort vulnérables et les plus difficiles à travailler.

Beaucoup de moments tragiques de l'icône russe sont liés à cet inconvénient dû à la particularité technologique en question. L'intérêt que l'icône a suscité, en tant qu'oeuvre d'art, à la seconde moitié du XIXe siècle a déterminé la nécessité de procéder à la restauration de ces monuments. Un tas de chefs-d'oeuvre se sont posés en victime de la jeune restauration inexpérimentée qui, en recourant à des procédés barbares, a hâtivement procédé à leur décapage. Les expositions de restauration ont connu, au début de notre siècle, des succès triomphaux aussi bien dans notre pays qu'à l'étranger. La prise de conscience et l'évaluation critique de ce qu'on avait fait ont été ajournées pour plusieurs décennies. Après le triomphe des années 20 et 30 l'attitude envers l'icône change ce qui est dû aux pertes importantes.

L'essor national dans l'économie et les arts, après la Seconde Guerre Mondiale, a également concerné l'icône. On voit s'ouvrir, dans les années 50-60, des ateliers qui avaient été fermés auparavant; on voit paraître plusieurs éditions illustrées consacrées à l'icône, éditions qui furent très demandées; on ne parle de la restauration qu'avec emphase. Le prestige du restaurateur à cette époque-là est hautement relevé, on entend souvent dire qu'il est "coauteur" de l'artiste peintre ancien. Alors on sous-entendait que tout ce que faisait le restaurateur n'était que pour de bon. L'idée qu'on peut nuire à tel ou tel monument lors de sa restauration fut exclue. On n'admettait point la possibilité même d'un endommagement quelconque. On prétendait

à l'irréprochabilité de l'intuition et de la maestria du restaurateur. Donc il est bien naturel que dans une telle atmosphère s'épanouissaient la reconstruction et le penchant aux retouches.

Cette atmosphère de satisfaction universelle sur la marche des affaires dans le domaine de la restauration des icônes fut troublée en 1961 par la Conférence de restaurateurs organisée au niveau de l'Union par l'Institut de recherche pour la restauration de l'URSS. Ladite conférence a produit un effet de choc et suscité de vifs débats. Pour la première fois on a motivé, faits à l'appui, l'illégalité de la reconstruction de la peinture sur l'original même. Deux camps se sont formés: les partisans des ajouts, des mises sur ton, de la reconstruction et leurs adversaires. Malgré le caractère intransigeant des positions prises, l'opportunité de la tenue de la conférence était évidente. Ses résultats se sont fait sentir quelques années après: le nombre de partisans de l'attitude archéologique envers la restauration a commencé, ne serait-ce que lentement, à croître. Quant aux discussions, elles ne tournaient qu'autour des problèmes de reconstructions et d'ajouts, comme d'ailleurs auparavant, mais quant aux questions relatives à la technologie, elles ne faisaient pas à ce temps-là l'objet d'une discussion spéciale.

Au début des années 70 les chercheurs de l'Institut de recherche pour la restauration (VNIIR) se sont convaincus, en le prouvant pratiquement, que l'enlèvement inoffensif de repeints multicouches est impossible sans microscope, quelle que soit la qualification d'un exécutant et indépendamment de l'expérience acquise. Il est à noter que c'est le professeur S. Toropov, chimiste ayant travaillé dans la restauration, qui a compris le premier toute la complexité et le danger que présentait le processus d'enlèvement des couches superposées pour la couche picturale originale. En 1934, il a fait paraître son article dans lequel il fournissait des arguments probants en faveur de l'utilisation du microscope lors de la restauration des icônes. Cet article n'a pas perdu sa signification de nos jours. Il a fort avancé son temps, mais à cette époque personne ne l'a entendu. Les restaurateurs d'alors, dont la plupart étaient peintres d'icônes, ne pouvaient qualifier ces dires sur microscope que de bizarreries d'un professeur qui ne "pigeait" rien à leur métier.

Ainsi, le VNIIR a dû tout recommencer dans les années 70 à partir de zéro, plus précisément, à partir de l'article ci-dessus du professeur Toropov, article qui fut écrit il y a 40 ans et bien oublié. Eh bien, qu'est-ce qu'il y a de changé dans la restauration des icônes depuis l'époque du professeur Toropov? Le plus important changement dans ce domaine concerne une large utilisation de divers solvants organiques et de leurs mélanges tandis que le restaurateur ancien ne se servait que de l'alcool et de la solution aqueuse d'ammoniac, humidifiait la surface de l'icône et enlevait une partie de repeints stratifiés au moyen d'un couteau. Les opérations se répétaient jusqu'à ce qu'il atteigne la peinture originelle. Cela faisant on abîmait souvent de concert avec le repeint des glacis minces, surtout des couches bouffies, on coupait les bords soulevés dans les endroits des craquelures, on ne réussissait pratiquement pas à conserver la dorure. Chaque procédé peut nous fournir de bons, de moyens et de mauvais exemples de tel ou tel travail, ce qui est fonction de la maîtrise d'un exécutant, mais décaper sans altérer et dénaturer est impossible lors de l'élimination de plusieurs couches superposées.

L'utilisation des solvants à partir des années 60 a rendu le processus de décapage plus facile mais pas moins dangereux. En amollissant les couches à enlever on amollit aussi la couche originale. Et si le restaurateur travaille à l'aveuglette, comme ses prédécesseurs, il nuit inévitablement à la couche picturale et, en fin de compte, dénature l'icône. L'analyse des surfaces des icônes décapées sans microscope prouve que chaque portion de la couche picturale représente une mosaïque très compliquée qui est composée d'une couche picturale intégralement libérée des encrassements et des repeints; de portions où les encrassements et les repeints sont partiellement restés; de portions où sont endommagés ou détruits des glacis minces, touchées des couches principales. En conséquence, la notion imposée sur les coloris et technique d'exécution de l'icône diffère fort de celle qu'on aurait pu avoir en voyant l'original. Ainsi, par exemple, on voit peu de bleu vif sur les icônes exposées aux musées, prédomine le vert de nuances diverses, cependant les maîtres d'alors suivaient la tradition et peignaient les tuniques, les manteaux, les toits de maison, l'eau en bleu. La disparition de la couleur bleue s'explique par l'imperfection du procédé de décapage: le pigment bleu se voit, pendant le processus de restauration, imbibé de l'huile de lin cuite diluée et se transforme optiquement en couleur

verte. Remédier à ce défaut par une restauration réitérative se révèle aujourd'hui impossible vu la complexité du processus qui exige beaucoup de main d'oeuvre. Bien sûr on se chargera de ce travail à l'avenir, mais actuellement il ne nous reste qu'à rétablir en imagination le coloris originel. Tous les endommagements, toutes les modifications et erreurs se produisent inconsciemment, car l'oeil non armé du restaurateur ne distingue pas les éléments nécessaires de la facture de surface picturale. On ne saurait dire que les restaurateurs ne connaissaient pas le microscope avant les années 70. Presque chaque atelier en possédait. Mais soit on ne les utilisait pas, soit on s'en servait très rarement. Quant à l'exécution des opérations de restauration sous microscope, on n'y pensait point. Mais substituer la loupe au microscope est impossible.

L'élimination des repeints à l'aide d'un stéréomicroscope représente, au fond, un processus tout à fait autre de restauration offrant une qualité très supérieure. A un grossissement moyen de 12-25^x, l'oeil du restaurateur distingue des glacis minces, des lignes, des coups de pinceau, des particules de pigments, donc toutes les opérations d'élimination de repeints multicouches se font consciemment. Au lieu du bistouri on se sert de micro-instruments à partir d'alliages durs représentant des tiges affûtées sous divers angles avec une partie tranchante de 1,5 à 2 mm. A l'heure actuelle les restaurateurs les fabriquent eux-mêmes.

En cas de travail avec le microscope on n'a pas besoin d'appliquer de compresses avec solvants; on n'a besoin que de quantités minimes de solvants pour enlever des repeints superposés, car tout matériau, y compris des couches très dures de vernis et de peintures anciens, est ductible sur une microportion. A propos, cette propriété des matériaux est exploitée par un des arts, notamment par la microminiature: exécution sous microscope de divers dessins et inscriptions sur métal, verre, matières plastiques, grains de graminées, etc.

A partir des années 70, l'enlèvement des couches superposées sur les icônes et les sculptures polychromes ne se fait dans le VNIIR qu'avec les microscopes. Ceci permet de conserver la couche picturale originelle sans défauts. Maintes fois les résultats de travail ont fait l'objet de plusieurs démonstrations et discussions. On a fait paraître beaucoup de publications à ce sujet. Les avantages, comme il le semble, sont évidents; néanmoins, parmi les centaines de restaurateurs s'occupant de la peinture de chevalet, il n'y a que 30 personnes au maximum qui pratiquent cette méthode dans le pays. Où en est la cause? Tout d'abord c'est une barrière psychologique - la crainte de passer à un autre régime de travail pour les yeux, régime non familial -, le sentiment de satisfaction sur les résultats du travail de restauration de nos jours, le désir d'éviter de compliquer son travail, de réduire sa cadence, ce qui peut avoir pour conséquence la diminution des rémunérations vu les normes en vigueur actuelles. Chose importante, les médias n'ont jamais donné une analyse objective et circonstanciée sur la situation actuelle dans le domaine de la restauration. Récemment encore on ne parlait de la restauration qu'avec admiration. Ces derniers temps quelques critiques sévères ont été adressées à la restauration architecturale, mais c'est plutôt le tribut à la mode. Quant à la peinture, on croit, apparemment, que tout va bien.

Le niveau de notre restauration, jusqu'au milieu des années 70, a été déterminé par les restaurateurs de musée. Mais durant ces 10-15 ans la situation a changé. Beaucoup d'organisations de restauration sont apparues dans le pays. La plupart de ces organismes sont commercialisés et se trouvent sous les ordres de divers centres. Ainsi ces organisations ont échappé au contrôle d'où l'existence simultanée de principes et de quelques modèles du processus de restauration, les uns excluant les autres. Il y a quelques organisations d'avant-garde qui vont de l'avant, elles ont bien devancé leurs collègues. La différence entre la qualité de leur travail et celui des autres, à noter qu'ils sont plus nombreux, est importante. Malheureusement les musées ne prennent pas conscience de ce fait, on n'attire pas l'attention des critiques d'art et des centres méthodiques à ce problème, tandis que leur participation a considérablement amélioré l'état de choses dans le domaine de la restauration de la peinture murale à l'échelle de tout le pays. Les musées veulent restaurer les icônes à tout prix sans y voir aucun risque. Le plus souvent cela s'explique par l'incompétence de ceux qui décident quel objet est à restaurer et par qui. L'impatience et le désir de réviser le concept formé des critiques d'art, et d'ouvrir une nouvelle exposition, voilà par quoi sont guidés ces gens-là. Alors, le chiffre d'affaires de la restauration commercialisée au lieu de diminuer, s'accroît progressivement.

Il n'existe pas d'analyse scientifique dans la restauration commercialisée massive; elle est remplacée par une appréciation gustative par analogie avec l'oeuvre artistique. Les objets restaurés ne sont pas soumis à l'expertise en vue de la détermination de la qualité du travail à cause du manque d'équipement technologique moderne et de moyens de contrôle optiques. Le danger réel existant dans la situation actuelle et menaçant les monuments de détérioration exige de prendre des mesures urgentes pour la solution des problèmes de conservation des oeuvres d'art du Moyen Age. L'idée de refuser le décapage et de concentrer tous les efforts sur la conservation des icônes dans les réserves des musées a été exprimée plus d'une fois. C'est une bonne idée, mais espérer la réaliser est plutôt une chimère, car on ne saurait pas arrêter la machine de restauration totale déjà lancée. L'opération jouant le rôle principal pour la conservation d'un monument n'est pas éclatante en apparence, tandis que l'effet produit par le décapage est toujours fort impressionnant. A propos, la restauration intégrale et la reconstruction de la peinture rapportent aux organisations concernées et aux exécutants d'énormes bénéfices. Les méthodes de contrôle moderne et l'expertise, qui devancent les opérations de restauration, peuvent apporter une contribution considérable quant à la conservation des originaux et des peintures d'icône. Ces méthodes sont mises au point par le VNIIR, mais leur mise en application dans la pratique courante concerne le changement des rapports entre les restaurations de musée, de production et scientifique et, aussi, l'introduction de critères d'évaluation de l'état de conservation de la peinture durant le processus de restauration.

Les gardiens et les collaborateurs scientifiques de musée se sentent libres de la responsabilité pour tel ou tel monument lorsque ce dernier quitte les murs du musée et le confie totalement aux restaurateurs. Nombreux sont les collaborateurs de musée qui ont une vague notion des buts de la restauration, des limites admissibles de l'intervention sur le monument. Beaucoup d'eau a coulé depuis la tenue de la première Conférence des restaurateurs au niveau de l'Union. Nous avons maintenant une nouvelle génération de restaurateurs et de collaborateurs de musée et on commence à oublier le vent frais de la discussion de 1968; on voit s'affermir de nouveau les positions des partisans des reconstructions et des retouches. Cette année à Moscou, une exposition des icônes du XVIIIe siècle a été inaugurée dans le monastère Novodévitchi. Les icônes exposées sont en provenance de l'iconostase de la cathédrale de Smolensk de ce monastère. Leur restauration a demandé quelques décennies et d'importantes dépenses. Et qu'est-ce qu'on a eu comme résultat? Devant le regard stupéfait et interrogateur des spécialistes sont apparues des oeuvres presque intégralement repeintes; on dirait que ce travail a été fait il y a cent ans. Les restaurateurs qui ont exécuté ce travail représentaient la restauration commercialisée massive, d'où leur attitude: ils ne s'intéressaient qu'au gain. Et la retouche, la reconstruction et la dorure rapportent le maximum. Ce qui est étonnant dans cette situation, c'est la position des collaborateurs scientifiques et des critiques d'art du musée qui, apparemment, se montrent contents d'une telle restauration des icônes. Nous espérons que ce cas affreux et instructif, qui sort de l'ordinaire, fera l'objet d'une discussion sérieuse portant sur l'état des choses dans la restauration des icônes (et non seulement des icônes) et que nous réussirons enfin à attirer l'attention des critiques d'art et des restaurateurs sur les méthodes scientifiques de restauration. Dans la restauration, malheureusement, on ne fait jamais le pas en avant qu'après avoir commis et analysé une grave erreur.

Aujourd'hui, le restaurateur a le droit moral de procéder aux travaux de restauration seulement lorsqu'il s'est assuré qu'existent toutes les conditions nécessaires garantissant l'absence de tout danger pour le monument. Quant aux collaborateurs scientifiques de musée, eux aussi doivent être certains de ce qu'on a pris des dispositions indispensables visant à assurer une bonne qualité des travaux de restauration. On entend souvent dire qu'on ne peut pas attendre jusqu'à ce que ces conditions soient créées, il faut agir vite pour sauver les monuments. Il en était ainsi de tout temps et toujours les plus graves préjudices ont été portés par une restauration hâtive et mal équipée. Ici il est question des icônes. Mais dans notre pratique quotidienne nous ne voyons pas de différences substantielles dans le processus d'enlèvement de repeints qu'il s'agisse d'icônes, de sculptures polychromes ou d'autels gothiques tardifs. La restauration des objets énumérés est confiée dans notre institut aux mêmes restaurateurs. Les peintures d'autel ouest-européennes et les sculptures polychromes sont aussi vulnérables que celles des icônes russes. C'est pourquoi tout ce qu'on vient de dire ne se rapporte point à l'icône russe ou à quelque chose d'autre, cela concerne la restauration en son

ensemble. Il faut noter que les collections d'icônes étrangères réunissent en général des monuments datant des XVII-XIXes siècles qui sont réalisés en techniques mixtes et sont ainsi plus vulnérables. Pour conclure je veux dire qu'il serait faux de se représenter la restauration des icônes en Russie comme une méthode russe unique. Les critères et la qualité sont différents chez nous, des principes communs sont encore à élaborer. Pour l'heure actuelle, la situation méthodologique est fort embrouillée. Par exemple, récemment à Moscou on a vu paraître un manuel sur la restauration des icônes. Les spécialistes soviétiques ainsi que leurs homologues étrangers brûlaient du désir de l'acquérir. Et non sans raison: on comptait que ce manuel refléterait le niveau contemporain dans la matière. Vains espoirs, c'est le jour passé de notre restauration. Nous considérons comme une tâche des plus urgentes de faire paraître un manuel qui reflète la manière scientifique d'aborder le problème de restauration des icônes russes.

Conclusion

Le présent rapport représente une tentative de faire une analyse de la situation actuelle, qui s'est créée dans le domaine de restauration des icônes en URSS, à partir des positions du VNIIR et en vue d'élaboration des voies de son amélioration.

RESUME

Analyse des changements méthodologiques dans la pratique de l'activité de l'Atelier de restauration des peintures russes anciennes du Musée Russe et de leur conformité aux principes fondamentaux de la restauration scientifique. Comparaison des résultats du décapage des icônes par les méthodes d'autrefois et adoptées récemment. Tendance de limiter l'utilisation des solvants pendant le décapage des monuments et son argumentation. Rôle de la technique d'exécution dans la structure artistique des icônes. Etude des oeuvres de la peinture russe ancienne comme un complexe d'investigations technico-technologiques, d'histoire de l'art et iconographiques. Application pratique de ce principe lors de la restauration de l'icône "Boris et Gleb" du XIV^e siècle.

MOTS-CLES

Décapage, étude, méthode, couche picturale, repaint, iconographie.

CERTAINS ASPECTS DE LA METHODOLOGIE DE RESTAURATION ET DE L'ETUDE DES PEINTURES DE CHEVALET EN DETREMPE DANS LE MUSEE RUSSE

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L'Atelier de restauration des icônes a été organisé en 1898, date de la création du Musée Russe. Les premiers restaurateurs, issus des peintres d'icônes héréditaires, étaient les maîtres Tchirikov, Tuline, Briaguine et N.Ia. Tchelnokov. Ils ont créé la base de la science future, élaboré les principes généraux de restauration. Certaines règles, formulées alors sont actuelles dans la pratique d'aujourd'hui:

- Nécessité d'étudier une oeuvre avant son décapage et d'établir une documentation détaillée.
- Interdiction des renouvellements sur les pertes des fragments de l'oeuvre pour ne pas apporter de subjectivisme.
- Mise sur ton neutre sur les lacunes pour ne pas empirer la perception du monument.
- Conservation dans les cas particuliers des renouvellements ou de leurs éléments.
- Utilisation pendant le décapage des matériaux inoffensifs pour le monument (1).

Cependant cette idée fondamentale de l'innocuité des matériaux utilisés et l'appréciation des résultats des travaux se modifiaient dans le temps et, naturellement, la méthode du décapage se transformait elle aussi.

Depuis peu le procédé courant d'enlèvement des repeints et de l'huile de lin cuite se passait comme suit: une compresse imprégnée de solvant était appliquée sur la surface d'une icône et après l'amollissement de tous les repeints, ils étaient éliminés à l'aide d'un tampon d'ouate et d'un scalpel chirurgical. Avec cela on utilisait souvent les compresses de grandes dimensions, les solvants agressifs et les expositions trop prolongées des compresses. Outre cela, tous les scalpels médicaux utilisés habituellement sont trop grossiers pour travailler les surfaces ayant le relief typique des monuments de la peinture russe ancienne (on sous-entend la facture de la couche picturale et le soulèvement de ses particules le long des craquelures).

L'expérience de travail dans l'atelier depuis de nombreuses années démontrait qu'actuellement une attitude pareille envers le processus de décapage n'est pas suffisante; beaucoup d'aspects de procédés de vieille date ne nous satisfaisaient pas. Le facteur subjectif jouait un grand rôle et avec cela, la qualité des travaux était moyenne. Quels que soient le zèle et l'expérience du restaurateur, ses possibilités étaient limitées et les endommagements inévitables. Outre les destructions mécaniques de la surface picturale par des outils de faible sensibilité, il est impossible d'éviter l'influence des solvants sur la peinture d'auteur. Ils pénètrent profondément par les fissures des craquelures, et si la couche picturale originale est affaiblie ou en mauvais état de conservation, elle s'émiette et quand on commence à faire le nettoyage, les pertes apparaissent dans ces endroits. Outre cela, la compresse avec solvant, ayant une capacité d'extraction, "tire" le liant de l'épaisseur de la couche picturale d'auteur, imprégnée d'huile de lin cuite, qui la lie davantage. Ainsi, la solidité d'adhésion entre les particules du pigment se voit brisée, les propriétés optiques de la peinture et, par conséquent, notre perception, se modifient, ce qui amène logiquement à l'altération de la conception d'auteur, contre laquelle se prononçaient tous les théoriciens de la restauration. L'importance de ce problème s'accroît toujours vu la compréhension du caractère symbolique des procédés techniques différents des maîtres anciens (2).

Ces observations furent la cause des changements dans les travaux de l'Atelier, qui étaient orientés vers l'utilisation des solvants de plus en plus "ménageants" et à la réduction des secteurs traités. Vers le milieu des années 1970 cela a amené à l'utilisation dans la pratique quotidienne du microscope binoculaire et à l'arrêt d'application de tout solvant quand on s'approche de la surface de la peinture authentique.

A la fin des années 1970 une méthode nouvelle de décapage était définitivement élaborée. D'abord sur un petit secteur du décapage d'essai, fait sans solvant, à sec, on tire au clair les particularités de la technique d'exécution, la composition des pigments et la succession des repeints. Sur les icônes faites avec l'utilisation des colorants peu résistants aux solvants, le



Icône "Boris et Gleb",
milieu du XIV^e siècle



Fragment de l'icône
"Boris et Gleb".
Manteau de Boris

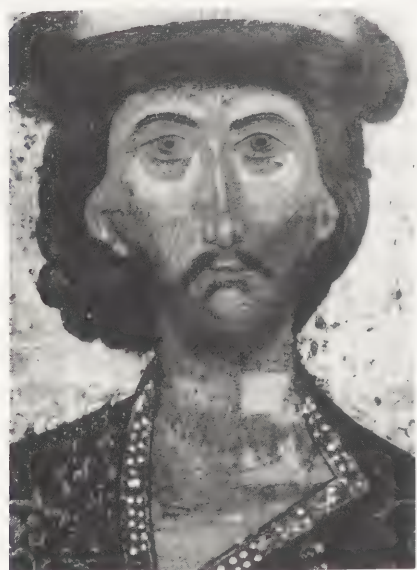


Image de Boris après
la restauration

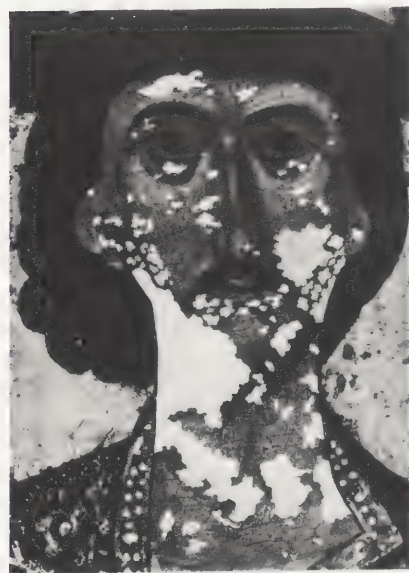


Schéma des pertes sur
l'image de Boris

décapage est poursuivi également à sec avec l'amincissement progressif des couches postérieures à l'aide du microscalpel spécial et l'humectation insignifiante de la surface par térébenthine. Lors du décapage des icônes faites à l'aide des pigments stables et ayant une couche considérable d'huile de lin entre le repeint et l'original, on admet une action de courte durée du solvant pour amollir les couches supérieures du repeint. Le travail dans les couches minces à proximité de la peinture d'auteur est fait à sec, comme décrit plus haut. L'exécution de toutes ces opérations sous microscope est une condition obligatoire.

Le ralentissement du rythme de travail, la possibilité de contrôler constamment la surface sous microscope ont permis de déceler certaines particularités dans la technique d'exécution, dépassant les cadres des conceptions traditionnelles, d'ouvrir la présence des couches de glacis extrêmement minces et l'utilisation dans la structure picturale des vernis colorés et des colorants organiques dont la sensibilité aux solvants étaient tellement grande qu'ils ne pouvaient pas être décelés auparavant.

L'icône la plus intéressante de ce point de vue est "La Sainte Vierge avec enfant sur son trône et St Nicolas et St Kliment" de la deuxième moitié du XIII^e siècle, provenant de la région de Novgorod. Avant tout, ce sont les visages des saints qui attirent l'attention: ils sont comme luisant de l'intérieur. Une étude a démontré que l'effet de cette perception était occasionné par la technique de leur exécution. Ils étaient peints par un vernis transparent, sa couleur jaune-intense était obtenue grâce à l'addition d'un colorant organique et tous les autres travaux de modelage étaient faits à l'aide de la détrempe sur cette couche de vernis. L'effet de luminescence douce était obtenu grâce à la réflexion de la lumière tombant de la préparation transparente. Le fonds des marges et certains autres détails de l'image étaient peints de la même manière. Une instabilité exceptionnelle même aux faibles actions des solvants était la particularité du vernis utilisé. Aujourd'hui il est impossible de définir l'étendue du champ d'application de cette technique dans la peinture russe ancienne de cette période, car les oeuvres décapées auparavant par les méthodes anciennes avec l'utilisation des solvants, ne peuvent pas être l'objet de comparaison pour pouvoir retrouver la technologie identique. Cependant, l'histoire de la peinture de l'Europe de l'Ouest connaît des exemples d'utilisation de la technique mixte similaire. La technique des peintures russes anciennes, la diversité des procédés employés par les maîtres anciens, reflétés sur les pages de nombreux ouvrages théoriques de nos collaborateurs, nous ont obligés à porter une attention particulière à leurs rapports avec la conception du monde, le symbolisme et la logique des monuments. Ainsi, un système d'investigations complexes des oeuvres se formait, incluant outre les études technico-technologiques, l'examen détaillé de l'iconographie des oeuvres et leur analyse dans le contexte iconologique. La comparaison de ces données avec les résultats des examens physico-techniques et de restauration donne des notions sur la structure artistique et logique de chaque icône - chose indispensable pour le restaurateur pendant son travail. La conception de restauration du monument ainsi que le choix des procédés de travail sur ces éléments isolés et, en fin de compte l'aspect du monument après la restauration, dépendent en grande partie de la profondeur de pénétration dans la conception d'auteur.

Le perfectionnement de la méthode d'étude et de restauration des oeuvres permet de résoudre des problèmes très compliqués. La restauration de l'icône "Boris et Gleb" du XIV^e siècle de la collection de N.P. Likhatchev (restaurée dans les années 1978 - 1988 par S.I. Goloubev) était un travail d'étape dans ce sens. Vu la nécessité de conservation de la couche picturale et multiforme, il a révélé de multiples fragments des repeints se rapportant à des époques différentes qui n'avaient pas été enlevés pendant la restauration de 1908, faite par les frères M.O. et G.O. Tchirikov. De plus, l'aspect du monument était considérablement altéré par des corrections de restauration faites avec une large superposition sur la peinture d'auteur, des repeints fragmentaires et des éclaboussures de couleur noire, des réparations et des mises sur ton faites par les frères Tchirikov, ainsi qu'une couche épaisse de vernis de protection légèrement coloré. Avec cela, beaucoup de détails effacés et perdus ont été repeints: les ornements des tissus, les plis des vêtements, etc. En tenant compte de tous ces faits, nous avons pris la décision de procéder à une restauration réitérative du monument.

N'ayant pour but d'élucider toute la marche des travaux, je voudrais m'arrêter sur certains points.

La difficulté consistait non pas dans l'enlèvement de toutes

les couches postérieures, mais dans le choix différencié entre ce qui devrait être enlevé et quels fragments pourraient être conservés afin de révéler au maximum la conception du peintre, car certains repeints, comblant les pertes, se sont déjà intégrés dans la peinture originale et leur enlèvement pourrait détruire l'aspect déjà formé de l'oeuvre.



Dessin calqué de l'image de Boris

Ce problème s'est posé pendant le décapage du dessin des vêtements des saints. Les ornements dorés et argentés qui couvraient auparavant les vêtements complètement, vers le moment de la première restauration étaient en grande partie perdus et repeints ensuite par les frères Tchirikov. Contrairement aux ornements d'auteur ils sont repeints par une couleur sombre à l'huile. Toutefois leur enlèvement pourrait transformer la composition artistique de l'icône. La parure dorée et argentée non seulement ornait les vêtements des saints, soulignant leur dignité princière, mais jouait son rôle important dans la formation de l'espace symbolique composé du monument. Les rapports de volume et d'espace de l'icône sont à peine perceptibles pour nos yeux, élevés sur les canons de l'esthétique classique avec ses trois dimensions. Le monde de l'icône - c'est un monde irréel, supersensuel, existant conformément à ses propres lois. C'est pourquoi Boris et Gleb sont peints sur fond complètement doré, symbolisant par son éclat le rayonnement de la gloire divine. Les figures des saints sont peintes dans un relief peu élevé et plat, reproduisant l'environnement conventionnel et immatériel, dont l'irréalité est accentuée par l'absence de la ligne d'horizon. S'appliquant à éviter complètement la matérialité de l'image, à détacher l'espace de l'icône du monde réel, le peintre a couvert les vêtements des princes d'un réseau d'ornements ajouré, brillant d'or et d'argent, qui rendait les couleurs légères et transparentes en les "diluant" dans l'or du fond. Les figures fragiles et immatérielles des saints sur l'icône semblent planer, transpercées par la lumière de la gloire divine. Cette image composée et profonde trouve ses parallèles dans la littérature russe ancienne. Glorifiant l'exploit de martyr de Boris et Gleb, Nestor, dans ses "Chroniques des temps passés" écrivait: "Soyez heureux, frères, dans la gloire impérissable... sous la lumière divine..."(3).

Sans doute les fragments perdus de l'ornement, repeints par les couleurs sombres, transformaient considérablement la conception initiale d'auteur, mais ils permettaient dans une certaine mesure de la restituer. C'est pourquoi lors du décapage tous ces éléments postérieurs étaient conservés.

Une analyse attentive de la structure artistique du monument nous donne une idée sur les changements intervenus dans son aspect le long des siècles de son existence. Dans ce sens le travail de décapage sur le visage de Boris est très intéressant. L'image représentait une combinaison complexe des fragments d'auteur et de multiples restes de repeints et de renouvellements de restauration. C'est pourquoi avant le décapage des visages et en se basant sur les résultats d'examen par les méthodes physiques on a établi les schémas détaillés de l'intégrité de la couche picturale. De plus, pour préciser le tableau des superpositions se rapportant à des époques différentes, on a accompli un grand volume de travaux pour révéler les analogies et les images typologiquement semblables parmi les monuments proches par le temps de leur création à l'icône en restauration. La comparaison a permis de faire une supposition, que les yeux, les sourcils, la barbe et la moustache droite sur le visage de Boris, repeints pendant la restauration de 1908, défiguraient considérablement l'image initiale du saint. Nous sommes dévisagés de l'icône par un regard tendu du visage désaxé et nerveux à barbe courte et pointue. La joue droite est un peu enfoncée, l'oreille est écartée avec affectation. Ce visage ressemble très peu aux images de Boris sur les monuments du milieu ou de la deuxième moitié du XIVe siècle (par exemple: les icônes avec les images de Boris et Gleb montés sur les chevaux, qui se trouvent dans la Galerie Tretyakov et le Musée de Novgorod). Il ressemble encore moins à l'image décrite par l'auteur de "Légende et souffrance et éloge aux Sts martyrs Boris et Gleb": "... Ce Boris... était beau par son corps, de haute taille, le visage rond... il avait de bons yeux... le visage gai...". Sur la reconstruction par analogie on n'a corrigé que la forme de la barbe du saint: elle était faite plus longue et éventailée. Même cette petite modification s'est avérée suffisante pour rendre à l'image du prince une expression nouvelle. La tension du martyr et l'aspect désaxé et nerveux cèdent place au courage, à la tranquillité et à la force spirituelle. C'est juste le portrait du prince qui nous parvient des sources littéraires. Le décapage du visage de Boris a confirmé les suppositions énoncées et la reconstruction proposée - un petit fragment de la barbe sous l'oreille droite du prince coïncidait presque complètement avec la reconstruction. Le nettoyage se passait avec le maximum de précautions et avec la



Dessin calqué - reconstruction de l'image de Boris

conservation des repeints sur toutes les pertes de la couche picturale originale. Vu l'absence de la peinture d'auteur, on a laissé sous les repeints les yeux, les sourcils et la barbe de Boris (4).

On a pratiqué des principes analogues pendant les travaux sur les autres détails de l'icône. La restauration nous a permis non seulement de consolider la couche picturale, mais elle a approfondi et enrichi nos idées de cette oeuvre unique.

Conclusion

A l'heure actuelle le perfectionnement des possibilités techniques de la restauration enrichit nos connaissances de la technique des peintures russes anciennes, de la diversité des procédés artistiques des maîtres anciens, ce qui nous fait penser à leurs liens avec la composition imagée de l'oeuvre. A son tour, cela donne une impulsion à la recherche de nouvelles voies dans le décapage, à l'élaboration de méthodes nouvelles. Sur l'étape des investigations, la corrélation des données matérielles et technico-technologiques avec la solution artistique et plastique d'auteur permettrait d'élaborer une conception précise de la restauration en conformité avec la conception d'auteur. Une attitude scrupuleuse envers l'étude de l'oeuvre avant le commencement des travaux de restauration est nécessaire non seulement par rapport aux oeuvres uniques, mais dans la pratique quotidienne. Il en résulte non seulement l'augmentation du niveau de la qualité des travaux, mais une compréhension nouvelle des oeuvres de la peinture russe ancienne.

Bibliographie

1. A.I. Anissimov. Principes scientifiques de restauration des monuments de la peinture. 1926. Département des manuscrits du Musée Russe, inv.6 unit 505
2. S.I. Goloubev. Technique de la peinture dans la structure artistique des icônes byzantins. - Culture matérielle de l'Est, Vol.2 M., 1988
3. S.I. Goloubev. Icône "Boris et Gleb" (catalogue d'exposition) p.11. Léninegrad, 1987
4. Ibid. p.13

CONSERVATION PROBLEMS IN EGYPT: ICONS
PRELIMINARY CLASSIFICATION & SOME CASE-STUDIES

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In 1988 a project "Restoration of Coptic Art" was set up with the aim of introducing interested Egyptians to the general principles and techniques of conservation and maintenance of icons. A short survey of the state of conservation of various icon collections in Egypt revealed that complete reconstruction of damaged icons - because of their continuing religious function - is still considered imperative. Unfortunately, the pious love for icons is generally greater than the scholarly knowledge about them. Most icons are cleaned and restored in the same way be they painted on wood, on canvas or on paper, in Greek, Coptic or Russian style and technique, ancient or nineteenth century.

(a) the native type which came into being in ancient times and
(b) the Greek type which is close to the Byzantine tradition.
This second type never completely replaced the first and older
one. Both existed side by side - together with some other
peculiar techniques.

Mediterranean sea

Alexandria

NITRIA

SCETIS

Cairo

Arsinoe

SINAI

St Catherine

Aphrodite

Sohag

Assuan (Syene)

Tabennisi (Keneh)

Nag Hammadi

Esna

Edfu

Syene (Assuan)

RED SEA

CHRISTIANITY IN EGYPT

Although the earliest known icons were, as is widely accepted, created in Egypt sometime between the 4th and 6th centuries - in the same encaustic and tempera techniques as the mummy and Fayum portraits -, today, in Coptic churches and monasteries there are not many icons which date back to an earlier period than the 18 c. (2).

MOTTO

Kurt Weitzmann,

I. Undated Icons

The oldest Egyptian icons have been studied and reports about their restoration have been published (3). Therefore we can pass on to the following phase and ask the question: were there medieval Coptic icons?

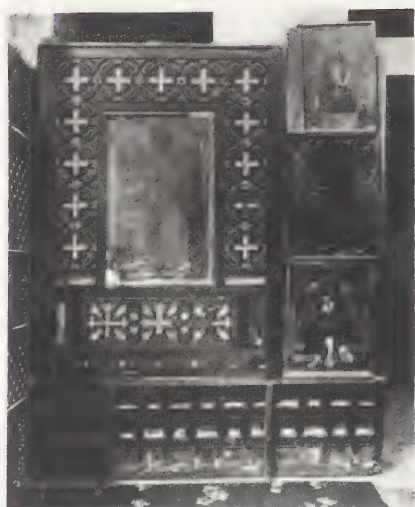


Fig.1 The icon of the Virgin with Child enthroned before any cleaning. Photo: from U. Monneret de Villard, *La chiesa di St.Barbara al Vecchio Cairo* (Firenze, 1922): fig. 17.



Fig.2 The icon of the Virgin with Child enthroned, after the last restoration in the eighties, in its original frame. The church of St.Barbara, Old Cairo. Photo: Z. Skálová, 1988.

The earliest icons emerging from the above mentioned gap of more than a millennium suggest a Sinaitic connection. St. Catherine's monastery on Mount Sinai preserved, thanks to its remoteness and the desert climate, arguably the most important collection of icons for the understanding of the icons in Egypt (4). This Greek community - connected by its metochia (branches) with important centres of icon painting in Constantinople, Cyprus, Crete, the crusader cities in Palestine and last but not least with cosmopolitan Jerusalem - became itself a transfer-centre of the import and export of icons and perhaps even for travelling izographs. There is some evidence - which deserves more thorough investigation - that Sinaitic art influenced not only medieval but also post-medieval Coptic icon painting (5).

Next to clearly imported Byzantine icons there are in particular at the left aisle of the church of St. Mercurios in Old Cairo five big icons which deserve special attention in this context.

(1) Nine Church Fathers and nine Coptic Monks flanking the Virgin with Child enthroned, (2) Twenty four Elders of the Apocalypse, (3) Six Coptic equestrian Saints, (4) Seven Coptic Martyrs, (5) Ten Feasts from the Life of Christ.

Their iconography is partly Byzantine and partly typically Coptic, their style and technology are Byzantine-Greek, the inscriptions are lost (6). They are executed in egg-tempera on gesso on huge, carelessly constructed panels, which are (partly?) overlaid with canvas covered with heavy cracked preparation layer of varying thickness, which extends to the borders. So does their gilded background. A definitive dating should be determined with caution, because some icons were overcleaned in the past, so that together with their original 'nomina sacra' also many details disappeared. Others are not yet properly cleaned. They may be compared with middle-Byzantine icons in the church of the Transfiguration at St. Catherine's monastery in Sinai, which are, alas, not yet fully published.

Some case-studies

Case 1: The icon of the Virgin with Child enthroned

It was possible to scrutinize one comparable icon of the same general, technical and stylistical characteristics which is presented here in detail. The icon of the Virgin with Child enthroned (125 x 76,5 x 2cm) is attributed to the 13th c. on the basis of comparison with icons at St. Catherine. Dr. Hunt concludes "that it is work of a Greek painter, conceivably undertaken at Sinai, but just as possibly imported from a Byzantine centre" (7). To my opinion the way in which the panel is constructed: a rather cheap, provincial, careless method if compared with contemporary icons from important artistic centres is an argument that this big icon was made in Egypt. (See fig. 3).

The panel consists of three vertical parts kept together by three traverses, which are on both ends about 6cm longer than the icon itself. They were obviously made to fit a frame (See fig. 4). The joints of the carelessly cut planks are filled with plaster and covered with a layer of palm-leaf fiber (8) which again is covered with the same plaster. This did not prevent splitting off so that the painting is disfigured by rifts that run from the top to the bottom along the joints. Another disfigurement was caused by large headed nails, 1cm in diameter, which were driven through from the front to fasten the traverses. The corroding iron nail-heads caused the canvas to rot and the gesso to fall off from above the heads which slightly protrude (9). Except these mechanical damages and unusually huge cracks which are probably also due to a careless methodology, the paint layer withheld the vicissitudes of centuries surprisingly well preserved.

An old photograph from the twenties shows that this icon was not tampered with until that time (See fig. 1). Such a remarkable state of original preservation must be due to specific conditions in Egypt: dry climate, no tradition of excessive religious 'refreshings' or overpaintings, and last but not least the placement in a case away from adoring fingers.

The icon of the Virgin with Child enthroned is displayed in the church of St. Barbara in Old Cairo in a heavy frame, which arguably was made for it in the 14th century (10) (See fig. 2). This would indicate that this holy picture as well as its typically Coptic frame have been in the same church ever since that time. It is not the only Byzantine icon which is set in such intarsia woodwork made for it.

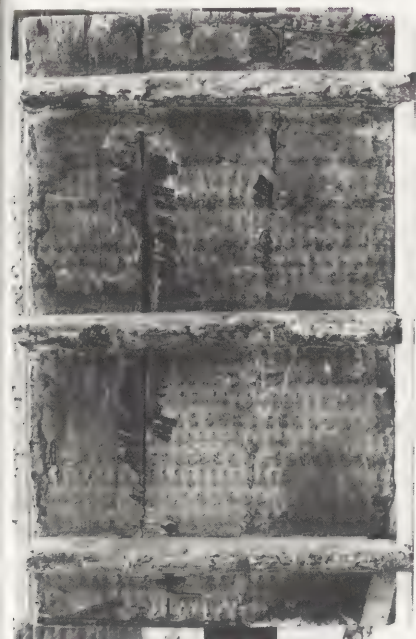


Fig. 3 The reverse side of the icon of the Virgin with Child enthroned, showing the protective layer of plaster with a green and red ornament. Among the numerous Middle-Byzantine, the 12th and 13th c. icons at St. Catherine's monastery at Sinai, there are a number of panels which have the same ornament on the reverse side. This seems to be a unique trade mark of the Sinaitic atelier as the pigments are local.
Photo: Z. Skálová, 1989.



Fig. 4 The icon of the Virgin with Child enthroned. Detail of the protruding end of one of the traverses which enabled the fastening of the icon in its frame.
Photo: Z. Skálová, 1989.

The aniconic, floral and geometric abstract decorations on these elaborate frames and altar screens which were doubtless intended to enhance the holy images within them are reminiscent of comparable ornamental designs on medieval Russian iconostases and Royal doors. The specific eschatologic significance of such symbolic ornaments - the promise of future life in paradise - used to be clear to the medieval believer, but it has been forgotten today (11). The combination of these ancient Byzantine icons and their original Coptic woodwork settings is so unique within the 'dissecta membra' of the Byzantine heritage as such, that they both deserve a most careful maintenance.

This group of icons can be safely restored according to modern Italian and Greek methods. But the painted surface was often damaged to the extent that in some areas it is difficult to recognise what the original detail was without a sound knowledge of the iconography. Moreover any further cleaning should be carried out under a microscope. The removal of later repairs will necessitate the reconstruction by an experienced specialist in this field, with water colours only.

Case 2: Icon within an icon

Another case history is the huge church icon of St. Mercurios with 16 scenes from his life (140,3 x 104 x 2cm) in the church of St. Mercurios Abu Sefein in Old Cairo (See fig. 5). This is a rare conjunction of two icons of different styles. A Byzantine icon of merit, executed in above mentioned Greek technique - now strongly overcleaned - has been used as a frame (polje) for a smaller icon of St. Mercurios, (93 x 56cm), an unorthodox looking oriental picture in unusual technique (see below). Neither of the two parts of this typically Coptic subject can be called Coptic, although both parts of the icon were most probably painted in Egypt. Both icons look equally shabby. Some questions arise: Which icon is older? Are these icons contemporary? Are the scenes from the Saint's vita those of the life of the martyr Mercurios? Is this an old restoration by a Coptic craftsman, who used a damaged icon with a narrative cycle of the life to enhance didactic function of this venerated icon of the church patron? The panel reverse is also interesting (See fig. 6). It shows similar characteristics in construction and use of materials as the icon of the Virgin with Child enthroned in the church of St. Barbara. The placing of protruding nail-heads suggest that the frame (polje) part of icon is nailed on another panel of the same proportions which created an effect of a deeper central part.

Not yet attributed icons on paper

In the same church of St. Mercurios there are more such 'oriental' icons. Their iconography meets the Coptic demands, but they remain strangely alien and distinguished. Their inscriptions are in Arabic. Some of these icons are painted directly on canvas support without any preparation layer, but most of them are executed on paper which replaced the priming.

Case 3: The icon of St. George

The most revealing from this group is the monumental icon of St. George (156 x 140cm), (See fig. 7). Leaves of paper from some old manuscript are glued to canvas which adhere to the wooden support. The question here of whether we are dealing with pages of a Christian manuscript with a special holy function, or a time-saving technique, or a traditional Eastern technology, remains open at this stage of research. A Linguist and an Arabic calligrapher could help to interpret and date these pages and the ornate inscriptions and consequently this enigmatic group of unknown icons.

The actual paint layer is applied directly on paper. The painting technique is rather simple, being usually made of one paint layer for incarnation and robes. Dark hues were obtained with coloured varnishes which suffered from unsensitive cleaning as did lavish ornament in gold and silver leaf which was applied in a too delicate procedure. The pigments are mixed with an organic binding medium composed of proteinous materials and sugars suggesting that the binder was probably a mixture of an animal glue and a vegetable gum (12). The palette is limited, being composed mainly of the basic pigments: very roughly ground orpiment, carbon black, white, red ochre, burnt ochre, unidentified dull green and their mixtures. In particular it has been observed that there is no blue pigment.



Fig. 5 The icon of St. Mercurios, Abu Sefein, with sixteen scenes from his life (?) The church of St. Mercurios, Old Cairo.

Photo: Z. Skálová, 1990.



Fig. 6 The icon of St. Mercurios. The reverse side. Photo: Z. Skálová, 1990.

It should be pointed out that the panel of St. George is made in a similar way as the above mentioned Virgin with Child enthroned and St. Mercurios so that the paint layers, although of different substance, manifest a comparable damage. Another common feature is a typical narrow raised frame made from strips of wood nailed to the front of the panel. This technical procedure obviously did not change for centuries (See figs. 3, 5 and 8). Therefore, this is not decisive for the date of the icon, but at the same time it must be taken into consideration. The challenging question arises: Are these icons more or less contemporary?

All this indicates a collaboration of native Coptic craftsmen, who prepared the panel, and a foreign painter who introduced his style and specific tempera technique. The creator of this 'school' of icons might have belonged to one of the Oriental Churches which for centuries flourished in central Asia and Asia Minor. It is probable that he was a monk, a scribe and illuminator of manuscripts, originally or simultaneously, working in a scriptorium.

It is to be hoped that these enigmatic icons - as there are many more scattered around the country - should be recognised by potential restorers as icons painted in a very vulnerable way which should be treated with utmost caution. They might appear, in course of further research, to have preserved an artistic tradition which - yet unknown to us - otherwise has almost entirely perished (13). A suitable conservation treatment is being researched in collaboration with the restorers of paper.

II. The post-medieval icons

The bulk of late icons in Egypt which can be with certainty attributed to the 18th and 19th c. can be again divided into two distinct groups: imported and truly Coptic. But according to the inscriptions - in Arabic and Coptic - many icons belonging to this second group were painted by Greeks or Armenians for Coptic patrons. They are the best ones.

From the technical point of view this local production can be split into:

(a) the art of the 'hinterland' with all characteristics which can be traced back to the mummy and Fayum portraits and even to the mummy coffins of the pharaonic period, executed traditionally simply and quickly in various kinds of tempera medium on the panel or canvas support; and

(b) the more urban style, influenced by Post-Byzantine Greek production, probably in cosmopolitan Cairo (See figs. 9 and 10). Although more sophisticated in style, the technology of these holy pictures can be again traced to the techniques used by ancient Egyptians: rude panels made from local wood, use of flax canvas covered with priming of various thickness, usually made from local materials such as gypsum, unslaked lime, anhydrite. The local pigments are hand ground and mixed in all kinds of medium. The gilding is obtained with gold leaf or powder applied directly over the preparation layer, which does not secure burnishing and leaves the surface matt. The adhesive might be garlic, egg-white, sugar or various glues and gums. Varnishes vary as in the ancient times. Some icons look as if they were not varnished at all which leaves their surface not only matt but unprotected. They often become powdery.

The gradual decline in the art of icon painting everywhere also occurred in Egypt. Hence, hastily executed Post-Byzantine icons are often in a worse state than much older works created according to old canonical processes, frequently leading to inaccurate datings. By the 19th c. icons were reflecting the confusion which accompanied the westernisation of Egypt. This resulted in the production of holy pictures, mostly on canvas, which gradually lost their emphasis on local subjects, their traditional technique - and finally their beauty and spirituality.

III. Conclusion

1) Restoration of icons painted in the Byzantine and the Post-Byzantine (Greek) tradition is very well documented and therefore pose no problem.

2) A responsible conservation treatment and cleaning methods for icons painted on paper is being studied. An interdisciplinary research will be organised and the results will be published at the end of this project in the spring of 1991 in a manual on restoration of Coptic icons.



Fig.7 The icon of St. George. The church of St. Mercurios, Old Cairo.

Photo: Z. Skálová, 1990.

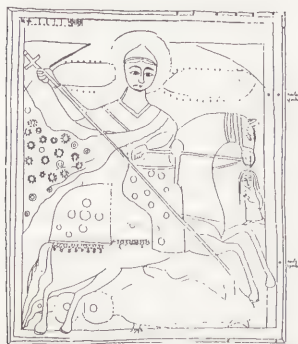


Fig.8 The icon of St. George. The reverse side.

Photo: Z. Skálová, 1990.

3) Icons which are executed on canvas have to be treated differently from those on a wood-support. A sound knowledge of the general principles of conservation & restoration of paintings is imperative. Relining with wax and resin mixture is not suitable for the hot climate of Egypt. The UNESCO paper mentioned in the note (1) offers to the practical application of some materials and methods.

4) About the treatment of the post-medieval Coptic icons some general conclusions can be drawn.

Although icons are, generally speaking, executed as egg-yolk tempera paintings, the Egyptian ones are not always true egg tempera. Local traditions survived. By using the same materials and technology as their ancient colleagues, the Coptic craftsmen left a testimony that an uninterrupted standard of workmanship was passed on from one generation to the other. Therefore, it can be assumed that there have been icons made through the total Christian era.

As there seems not to exist a distinct Coptic restoration tradition (14) - as it was, for example in Russia among the Old Believers - the training of specialists in this field is important. Coptic icons should not be treated haphazardly as familiar Greek, Italian or Russian ones, but rather as precarious Egyptian ethnographical objects. Each icon brings specific problems: the choice of materials used for conservation and cleaning should depend on the knowledge of its technique. But the considerable body of published material on ancient Egyptian art, executed in tempera, and its conservation offers unexpected and simple possibilities for a suitable conservation treatment for many Coptic icons.

NOTES

1. To my knowledge there is just one study about the conservation of Coptic icons, but it recommends treatment used in Italy by the Istituto Centrale del Restauro at Rome, which is suitable only for those icons which are executed on a flexible (canvas) support. See H.J. Plenderleigh, P. Mora, G. Toracca, G. de Guichen, "Conservation problems in Egypt"; Studies in Cairo, Section II: Report on the condition of icons examined in the Coptic churches of St. Sergius and St. Barbara and in the Coptic museum. (Unpublished, UNESCO Consultant Contract No. 33.591, Rome, 1970).

I would like to thank Paolo Mora of the Istituto Centrale del Restauro, Rome, who when in Egypt in February 1988, kindly shared his experience.

Z. Skálová, "Conservation problems in Egypt I: Preliminary report on the condition and restoration of the post-medieval Coptic icons", forthcoming in the volume on Coptic art in the series of the Netherlands Institute for Archeology and Arabic Studies, winter 1990. Cairo and Z. Skálová, "Some remarks on the technology of the post-medieval Coptic icons", forthcoming in *Bulletin de la Société d'Archeologie Copte*, XXVII, 1990, Cairo.

2. L. Hondelink-Langen & H. Hondelink catalogize the icon collections in the Coptic museum and elsewhere in Egypt under supervision of Prof. Dr. P.P.P. van Moorsel, Dept. of the Early Christian Art of the University of Leiden.

3. D.L. Thompson, *Mummy portraits in the J. Paul Getty Museum*, Malibu 1982; G.Z. Bykova, "Restavratsija enkaustičeskoj ikony Sergij & Bakch VI-VII st. iz Kievskogo muzea vostočnogo i zapadnogo iskusstva" *Chudožestvennoje nasledije* no. 32 (Moscow: VNIIR, 1977), 124-133;

4. K. Weitzmann, *Studies in the Art of Sinai*, Princeton 1982; K. Weitzmann, "Byzantine Miniature and Icon Painting in the Eleventh Century", in *Proceedings of the XIIIth International Congress of Byzantine studies*, (Oxford, 1966): 207-224. G. and M. Soteriou, *Icones du Mont Sinai I-II*, (Athens, 1956).

5. Weitzmann states that "the church in Sinai teaches us that in the early Eastern Church the feast pictures were not individual icons, but were painted on beams. In all the Orthodox world, only St. Catherine's has preserved examples of this ancient usage. See, K.W. Weitzmann, "Mount Sinai's Holy Treasures", in *The National Geographic*, vol. XXV, (1964): 119.

I refer here to the 18th c. beams of the feast pictures in the Coptic churches St. Barbara and St. Sergius in Old Cairo.



Fig. 9 The icon of St. Tekla, Himanot el Hoashy, A.D. 1739 in the collection of St. Anthony monastery near the Red Sea, before cleaning. The measurements: 68x43,3x1cm (without the frame). Photo: H. Hondelink, 1988.



Fig. 10 The same icon after the restoration. The cleaning of darkened varnish revealed the traditional Byzantine background-concept of divine light and earth sections. On this Coptic icon of an Ethiopian Saint the normally green earth section became the more familiar yellow desert. Photo: Z. Skálová, 1989.

The icons on photo's no. 3, 4, 5, 6, 7, 8, 9 and 10 are being published here for the first time.

6. A.J. Buttler, The ancient Coptic churches of Egypt, Vol. I. (Oxford, 1889) Reprint 1970: 104-108.

7. L.A. Hunt, "Iconic and Aniconic: Unknown Thirteenth and Fourteenth Century Byzantine Icons from Cairo in their Woodwork Settings", in Poikila Byzantina 6, Varia II, (Bon. 1987): 45.

8. For this use see: L. Lazzarini and P.M. Schwartzbaum, "The technological examination and restoration of the paintings of the dome of the Al Aqsa Mosque, Jerusalem", in Studies in Conservation 30, no. 3 (1985): 132.

9. For the similar technique see: D. Talbot Rice, Icons of Cyprus, (London, 1937): 91.

10. Hunt, "Iconic and Aniconic", 45.

11. L.A. Lelekov, Iskusstvo Drevnej Rusi i Vostok, (Moscow, 1978).

12. For this information I would like to thank Dr. L. Losos from the State Restoration Ateliers, Prague, CSR.

13. T.W. Arnold, Survival of Sasanian & Manichean Art in Persian Painting, (Oxford, 1924) and L.N. Gumil'ov, Poiski vymyslenogo carstva - Legenda o gosudarstve presvitera Ioanna, (Moscow, 1970).

14. Old and damaged icons were not restored but are said to be used as fuel for cooking holy mirrh. This tradition, which still continues, would also explain the absence of ancient icons.

Acknowledgement

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SELECTED BIBLIOGRAPHY

P. Amato, De Vera Effigie Mariae. Antiche Icone Romane. (Roma, 1988) Basilica di S. Maria Maggiore 18 giugno-3 luglio 1988.

J.G. Bobrov, Istoria restavratsii drevnjerrusskoj Zhivopisi (A survey of the restoration of the medieval Russian icons) (Leningrad '87).

S. Chojnacki, Major themes in Ethiopian painting (Wiesbaden 1983).

Icones Melkites: Exposition organisée par le Musée Nicolas Sursock du 16 Mai au 15 Juin 1969 (Beyrouth, 1969).

A. Lucas, Ancient Egyptian Materials and Industries, 3rd ed. (1948).

C. Mulock and M.T. Langton, The Icons of Yuhanna and Ibrahim the Scribe, (London, 1946).

K. Parlasca, Mumienporträts und verwandte Denkmäler (Wiesbaden 1966)

A. Weis, Die Madonna Platyttera. Entwurf für ein Christentum als Bildoffenbarung anhand der Geschichte einen Madonnenthemas. (Königstein im Taunus, 1985).

ABSTRACT

The technique of depicting a human face constitutes the most challenging part of icon painting. Comparison of lecture (Hesh) -- painting with "dolichnoe" -- painting of dresses, architecture background and landscape shows that human faces were executed in a more (objects) detailed and sophisticated manner: they had a greater number of modeling stages and paint layers. The faces seen in Byzantine and Russian icons look particularly complicated. Unlike them, wall and miniature painting were more frequently done using "shorthand" methods. However the painting procedure remained identical; in other words, it was layer-by-layer application. It is very difficult to investigate painting methods because they were masked and undetectable which was consistent with the basic esthetic ideas of the Middle Ages: icons could not be created by man. The method of optic examination of painting layers with the aid of a binocular microscope has been developed to help a restorer to uncover the original and to discriminate between the ancient painting and many overpaintings.

KEYWORDS

Optic, examination, "lichnoe", "dolichnoe", binocular microscope, painting technique, medieval layer-by-layer method, sequence of paint application, modeling of a human face, shorthand painting, recipes of medieval manuals.

APPROACHES TO THE STUDY OF METHODS USED IN MEDIEVAL FACE PAINTING

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Results and discussion

At present restoration of medieval paintings is to meet very stringent requirements which can be achieved, among other things, by a wide application of optic methods of quality control. The approach described in this paper allows improvement of visual examination of the painting structure. This approach helps to obtain necessary information. The approach is based on a strict order of stages of study correlated with the structure of paint layers and sequence of their application by a medieval artist.

The method presented here was developed on the basis of a thorough study of written sources - treatises and manuals of medieval fine arts - and their comparison with many Byzantine and old Russian icons from Soviet and foreign art museums (1). Out of 330 sources describing the painting methods published by Samuel Alexander (2), only three manuals present recommendations concerning human face rendition. These are: "Notes about Different Arts" by Theophiles that date back to the turn of the XII century, "Treatise about Painting" by Cennino Cennini published at the turn of the XV century and "Hermeneia" by Dionysios of Fourmy published in the XVIII century. The three sources give evidence that the artistic experience of their authors is based on the medieval layer-by-layer method.

The earliest recipe is that of Theophiles. The author indicates that he took his lessons from Greek masters; it can therefore be maintained that his recommendations are related to the painting patterns of the mid-Byzantine era. However the fact cannot be ignored that this is an interpretation offered by a Roman master and not an exact reproduction of Byzantine works. Theophiles emphasizes and recommends shorthand painting and simplified modeling methods.

The treatise by Cennino Cennini is a document of the Trecento period. It was created in Padova which, on the one hand, kept up the old traditions of Giotto di Bondone and, on the other, followed the artistic development of Venice where Byzantine tendencies were felt throughout the XIV century up to the middle of the XV century. This accounts for the diverse instructions Cennini offers for painting a human face. He describes shorthand methods inherited from Roman masters as well as many patterns of modeling layers that can be used both in wall painting and in board painting.

The last manual is Hermeneia created in the Athos monastery which canonized Paleologus painting techniques and formulated a universal scheme of drawing through different stages. This scheme formed the basis of the method presented here. It includes nine stages of creating an artistic form which corresponds to the use of nine different colours (see Table 1). The method of visualization and fixation of painting techniques allows discrimination of a far greater number of details and nuances than those reported previously (3). This method permits differentiation of modeling layers (first, second and third layers or ground, flesh and reddish colours), drawing pattern (preliminary, second and finishing), shades (colour shadow frame, shading lines) highlights (whitish strokes and touches). The method allows for not only colour shades but also the technique of their application.

Conclusion

The method presented in this paper helps a restorer to get properly oriented in a complex medieval painting covered by many overpaintings, to identify his target and to guarantee a high accuracy of documentation.

Table 1

Medieval techniques of face-painting

1. Preliminary drawing which is an original sketch applied to the ground. In a complete picture it was as a rule masked by colour layers applied onto it. In certain cases, mostly in icons, it showed up through overpaintings which exerted an impressive effect.
2. Priming layer which was covered with an overall ground colour. This was an intermediate colour shade that served as a background for the modeling layers to be applied later. In short-hand painting this layer was never overpainted and acted as the basic flesh colour. In pictures executed in a more detailed manner the ground colour was overpainted. If the ground colour was similar to the shadow frame, it was not covered with a lighter colour in the relief depressions or along the borders of the face; in this situation it acted as a shadow colour.
3. Second (repeated) drawing of facial features which was applied to reproduce the lines of the preliminary drawing above the ground colour which were still discernible to the painter.
4. Shadow colour which could be a layer of the overall ground colour that remained unpainted in the relief depressions. It could however be made additionally: lines of the second drawing were enlarged and shaded forming a shadow frame. The shadow colour depended on the drawing colour and could be either green or brown. At different stages the shades were repeatedly added.
5. First modeling layer which was applied to the protruding parts but not painted over the shadow colour. Sometimes the modeling layer became the principal colour in the face but was frequently used as a foundation for still lighter layers playing the part of penumbra.
6. Flesh colour which was lighter than the preceding first layer. It also belonged to the modeling layer but was applied only to the prominent forms. The flesh colour was typical of pictures that had not only colour but also tone contrasts.
7. Reddish colour which was applied to the selected parts of the face, i.e. lips, crest of the nose, cheeks, and dark parts of the forehead and neck. During the modeling process this colour was merged with shadows that were brown shades.
8. Highlights which finished the strongest prominent parts of the face. Depending on the modeling pattern, they were painted over either the ground colour or the first modeling layer and flesh colour. Sometimes there was another whitish shade between highlights and flesh colour. Highlights were applied in many different ways: as gentle spots or as strokes and touches.
9. Finishing outline which was applied either after or before the semi-transparent layer was painted. This was the most expressive method of medieval painting, particularly of short-hand painting. Its colour was correlated with the form varying from brown to black. The eye socket outlines were most multi-coloured. In the shaded parts of the face the outline coincided in terms of colour with the shades which transformed to the most densely packed areas of the drawing, thus making it harmonious and the face three-dimensional.

Bibliography

1. Yakovleva A.I. Techniques of ancient Russian painting (Pre-mongolian period). Abstr. Cand. Dissert., Moscow, 1987 (in Russian).
2. Alexander S.M. Towards a history of art materials - a survey of published technical literature in the arts. Art and Archaeology Technical Abstracts. 1969, vol. 7, № 3,4; 1970, vol.8, № 1.
3. Filatov V.V. Russian easel tempera painting. Technique and restoration. Moscow, Iskusstvo, 1960 (in Russian); Grenberg Yu.I. Technology of easel painting. Moscow, Iskusstvo, 1982 (in Russian); Winfield D.C. Middle and later Byzantine wall painting methods. DOP, Cambridge, Mass., 1968, vol. XXII, pp. 63-169.

TABLES 1

MEDIEVAL TECHNIQUES OF FACE-PAINTING

Preliminary drawing	An overall ground colour	Second (repeated) drawing	Shadow colour or "shadow frame"	First modeling layer	Flesh colour (second modeling layer)	Reddish colour (shading)	Highlights (semi-transparent layer, strokes, touches)	Finishing outline (shading line)
1	2	3	4	5	6	7	8	9

Working Group 24

Rock Art

Art rupestre

RESUME :

L'étude de l'abri orné de la Toca do Boqueirao da Pedra Furada, situé dans le nord-est de l'état du Piauí au Brésil, faite par analyse stratigraphique picturale des tracés peints et par analyse physique et chimique, a révélé que les pigments avaient été appliqués directement sur la roche (sans préparation de celle-ci). Les couches de pigments étaient minces et recouvertes en général de fins dépôts. Ils sont complexes et variés et les témoins plus ou moins disparus d'évolutions antérieures de la surface de l'abri. L'hétérogénéité des dépôts peut être une source potentielle de désordre des surfaces à tracés peints.

Mots-clés :

Brésil
Peintures rupestres
Stratigraphie picturale
Analyse physique
Analyse chimique



PREMIERS RESULTATS DE L'ETUDE DES PEINTURES RUPESTRES DE LA TOCA DO BOQUEIRAO DO SITIO DA PEDRA FURADA (PIAUI - BRESIL)

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1 - Introduction

L'aire archéologique de la région de São Raimundo Nonato est située dans le Nord-est du Brésil, plus précisément au sud-est de l'état du Piauí (voir figure 1). Les plateaux (Chapadas) sont des surfaces monotones, d'altitude moyenne entaillés de vallées. Dans ces vallées, le long des abrupts rocheux sont localisés des sites d'art rupestre.

Dans cette aire archéologique, la Mission franco-brésilienne du PIAUI sous l'autorité de Madame Niède GUIDON, développe un programme de recherches interdisciplinaires. Les résultats présentés ici trouvent leur place dans ce cadre, puisque l'une d'entre nous (Maria Conceição SOARES MENESES LAGE) prépare une thèse à l'Université Paris I sur : l'art rupestre du sud-est du PIAUI - BRESIL ; une étude archéométrique.

2 - Rappels sur l'art rupestre de la région

Dans l'aire archéologique de São Raimundo Nonato, les oeuvres rupestres sont réparties dans plus de 200 abris sous roche ; il s'agit essentiellement de peintures. Cet art est riche et varié, avec une abondance de motifs figuratifs et non figuratifs. Les représentations d'anthropomorphes sont très diversifiées : les corps peuvent être ronds, ovales, carrés, rectangulaires ou filiformes. La tête est en général ronde et les membres sont représentés par un trait ; les visages ne sont pas figurés et les pieds et les mains ne sont pas toujours dessinés. Le sexe féminin, moins représenté que le masculin, est formé d'un cercle ou d'un demi-cercle.

Les animaux sont en général des cervidés, des tatous, des nandous, des jaguars, des oiseaux, des lézards, des singes, des poissons et des cabiais. Il s'agit dans la plupart des cas d'espèces typiques de la région, ou d'espèces qui y ont vécu et ont maintenant disparu.

Les figures peuvent être associées, elles représentent alors des thèmes bien précis tels que des scènes de chasse, de relations sexuelles, de luttes, d'accouchements, d'acrobaties.

Les peintures sont exécutées avec différentes tonalités de rouge et on trouve également des figures peintes en jaune, blanc, marron noir et gris.

La technique de remplissage la plus couramment utilisée est celle de la teinte plate mais on trouve aussi d'autres types de remplissage : des points, des traits, des triangles, des carrés, des cercles, etc...

Les thèmes des gravures sont en général différents de ceux des peintures. Niède GUIDON, préalablement à cette étude, a classé l'art rupestre du sud-est du Piauí en traditions, sous-traditions et styles. Les traditions sont définies par le type de figures représentées et leur fréquence. Les sous-traditions sont liées à la répartition géographique et les styles aux techniques d'exécution des graphismes.

Le schéma de cette classification peut être trouvé dans différentes publications de la Mission franco-brésilienne du PIAUI sur l'art rupestre (N. GUIDON 1976, 1983, 1985 ; A.M. PESSIS, 1987).

3 - Le site étudié : la Toca do Boqueirao do Sitio da Pedra Furada

3.1. Description

La Toca do Boqueirao do Sitio da Pedra Furada (B.P.F., en abrégé par commodité d'écriture) est un abri sous roche avec une énorme quantité de graphismes qui couvrent un grand secteur de la paroi rocheuse. Selon la description de Bernadette ARNAUD (1982) c'est un site du type paroi de grande taille avec surplomb. Il se trouve dans un bas de versant à 12 m du fond de la vallée et à 7 km à l'ouest du village de Varzea Grande. L'abri mesure 70 m de longueur et la paroi a une hauteur d'environ 80 m.

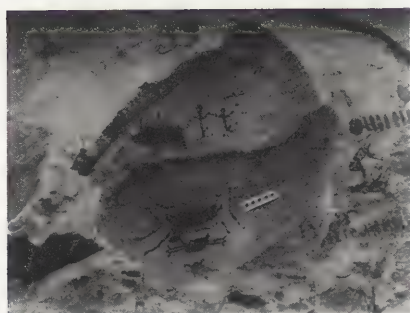
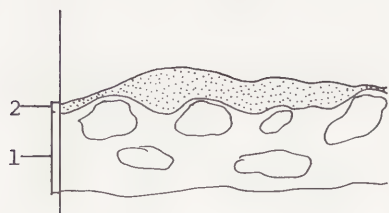


Photo 1 : Localisation du prélèvement B.P.F.35



Croquis 1 : Coupe stratigraphique du B.P.F.35

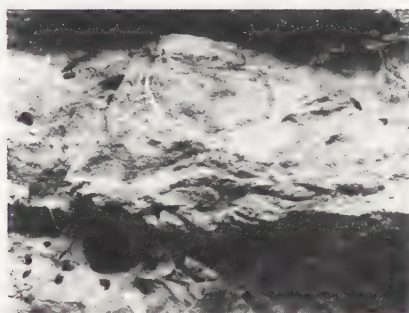
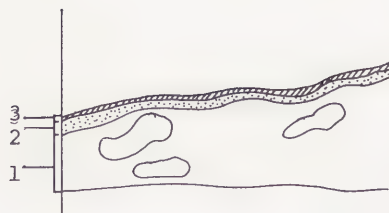


Photo 2 : Localisation des prélèvements B.P.F.38 et 39



Croquis 2 : Coupe stratigraphique du B.P.F.38

L'abri étant orienté est-ouest, c'est sur la face ouverte au sud que se situent les peintures. La plupart des peintures ont été exécutées à l'intérieur de niches naturelles de la paroi. Une grande partie des oeuvres a cependant été détruite par désagrégation de la paroi. Ce site a été fouillé depuis 1978 et une série de datations archéologiques a été mise en évidence de 17.000 B.P. à 47.000 B.P.). La plupart des peintures de ce site est du type figuratif (anthropomorphes et zoomorphes). Les couleurs identifiées sont le rouge, le jaune, le gris et le blanc.

Selon Joël PELLERIN "la série gréseuse détritique du front de cuesta est constituée à la base d'un grès feldspathique surmonté par un poudingue". Toujours selon le même auteur les parois des abris sont recouvertes d'encroûtements stratifiés très minces. La paroi était et est soumise aux phénomènes d'alvéolisation (formation de taffoni) responsables de l'aspect si caractéristique de l'abri du B.P.F. dont la surface possède des dépressions de dimensions métriques emboîtées les unes dans les autres. Les peintures sont tracées sur ce support très dur (d'où la difficulté de faire des prélèvements) ; compte tenu des possibilités d'évolution morphologique de la paroi, y a-t-il un risque de dégradation des surfaces ornées dans l'immédiat ou à moyen terme ?

3.2. Analyses

Ces études avaient pour but l'identification des pigments préhistoriques, la connaissance des relations entre les couches pigmentaires, la connaissance des produits d'altérations. Quarante-huit prélèvements ont été réalisés dans l'abri Toca do Boqueirao do Sitio da Pedra Furada, ils correspondent aux problèmes posés au niveau du support et au niveau des peintures. Ne seront présentés ici que les éléments les plus significatifs. Chaque prélèvement est repéré grâce aux références (figure et panneau) de l'inventaire de la Mission franco-brésilienne du Piauí.

3.2.1. Stratigraphie picturale de prélèvements

3.2.1.1. Descriptions des sections polies

Les coupes stratigraphiques sont obtenues par inclusion du prélèvement dans une résine polyester, sciage du bloc ainsi obtenu, puis polissage d'une section.

B.P.F. 35 :

Prélèvement de couleur dite "rouge foncé" de référence Munsell 10R 3/4, effectué sur une représentation zoomorphe (cervidé, voir photo 1) dont le contour ouvert est bien tracé et dont le centre du corps présente deux nuances de couleurs. Les colorants ont été appliqués par la technique du remplissage (teinte plate). Cette représentation zoomorphe porte le numéro 5 du panneau CCXXXVIII de l'inventaire.

A la loupe binoculaire le prélèvement révèle une surface irrégulière ; la couche du pigment rouge paraît relativement épaisse.

L'étude stratigraphique indique (voir croquis 1) :

- une couche blanchâtre (couche 1) correspondant au grès ; on distingue très bien les grains de quartz dans la roche
- une couche rouge d'ocre rouge (couche 2 d'épaisseur moyenne 43 µm), mêlée de petits grains de quartz détritiques ; cette couche est en général continue et plus épaisse dans les dépressions de la surface
- une couche fine, blanchâtre, continue (couche 3, épaisseur de 3 µm) de dépôt (non visible sur le croquis).

B.P.F. 38 :

Prélèvement de couleur dite "rouge clair" et de référence Munsell 10R 5/8, fait sur la partie ventrale d'une représentation incomplète de zoomorphe (cervidé ?, voir photo 2) dont le corps est constitué d'un double contour blanc (externe) et rouge (interne). Le zoomorphe porte le numéro 6 du panneau CCXLVIII de l'inventaire.

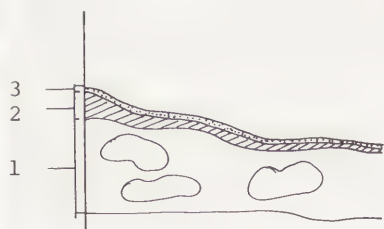
L'observation à la loupe binoculaire révèle la superposition d'une couche blanche sur le rouge.

L'étude stratigraphique permet de distinguer (voir croquis 2) :

- une couche blanche (couche 1) formée de grains de quartz
- une couche rouge d'ocre rouge (couche 2 d'épaisseur 5 µm) - une couche blanche (couche 3 d'épaisseur 3 µm) externe de pigment (peu visible sur le croquis).

B.P.F. 39 :

Prélèvement effectué sur la partie supérieure du contour blanc de la figuration citée précédemment (photo 2). L'examen du prélèvement à la loupe binoculaire révèle la superposition du rouge sur le blanc et l'absence du support rocheux.



Croquis 3 : Coupe stratigraphique du B.P.F.39

L'étude stratigraphique montre (voir croquis 3) :

- une couche blanche (couche 1) de dépôt sans matérialisation de la forme des grains
- une couche discontinue de pigment blanc (couche 2 d'épaisseur 12 μ m)
- une couche d'ocre rouge très fine et irrégulière (couche 3 de 1 μ m).

B.P.F. 22 :

Prélèvement de couleur dite "rouge foncé" correspondant aux références 10R 3/6 du code Münsell, réalisé sur une représentation d'anthropomorphe (voir photo 3) exécutée selon la technique du dessin. Cette figuration localisée dans une niche correspond au numéro 23 du panneau CCXXXIV de l'inventaire.

L'observation sous la loupe binoculaire de la partie colorée du prélèvement montre un aspect irrégulier avec des grains de quartz en saillies. La couche de matières colorantes rouges paraît relativement épaisse et surmontée d'un dépôt de teinte plus claire.

L'étude stratigraphique au microscope révèle trois couches (voir croquis 4) :

- une couche blanche (couche 1) où l'on différencie les grains de quartz ; c'est la partie arrachée au grès
- une couche rouge d'ocre (couche 2) d'épaisseur moyenne 39 μ m avec de très petits morceaux de quartz
- une couche blanche (couche 3 de 9 μ m d'épaisseur) très fine en surface (dépôt de poussières).

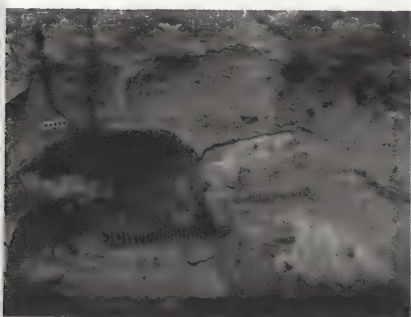


Photo 3 : Localisation des prélèvements B.P.F.22, 19 et 20

B.P.F. 23 :

Prélèvement effectué sur une représentation zoomorphe de couleur dite "rouge moyen" de référence Münsell 10R 4/8.

La technique utilisée est dite "teinte plate sans contour". Cette représentation zoomorphe - cervidé incomplet (voir photo 4) porte le numéro 48 du panneau CCXXXIV de l'inventaire.

Examiné à la loupe binoculaire au laboratoire, l'échantillon révèle une surface irrégulière et on distingue un dépôt blanc surmontant une couche rouge plus au moins foncée.

L'examen de la stratigraphie révèle (voir croquis 5) :

- une couche blanchâtre (couche 1) de grains de quartz
- une couche blanchâtre de dépôt (couche 2 d'épaisseur moyenne 145 μ m)
- une couche d'ocre rouge (couche 3) discontinue d'épaisseur inégale, d'environ 25 μ m.

On doit souligner l'absence en surface de couche identifiée habituellement comme couche d'altération. Y a-t-il eu dépôt puis érosion ou absence de dépôt ? Cette remarque n'étant valable que pour le prélèvement B.P.F. 23.

B.P.F. 47 :

Prélèvement de couleur blanche fait dans le corps d'une représentation de zoomorphe (lézard, voir photo 5) superposée à celle d'un autre zoomorphe (nandou). Le lézard a été tracé selon la technique du contour et d'un remplissage à traits contigus. Il porte le numéro 26 du panneau CCLXV de l'inventaire.

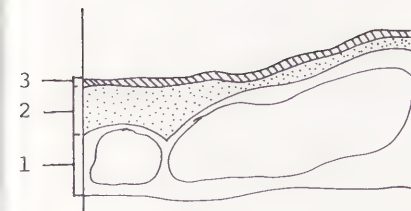
A l'oeil nu sur le terrain, et à la loupe binoculaire au laboratoire on remarque la superposition du pigment blanc sur le pigment rouge.

Au microscope, nous voyons (voir croquis 6) :

- une couche blanche (couche 1) constituée de grains de quartz
- une couche rouge (couche 2 d'épaisseur moyenne de 11 μ m) d'ocre rouge
- une couche blanche (couche 3 d'épaisseur 17 μ m) en recouvrement du rouge.

B.P.F. 43 :

Prélèvement pulvérulent de couleur grise correspondant aux références du code Münsell 5Y 7/1, effectué dans la partie centrale d'une représentation d'un zoomorphe de profil (cervidé) et dont le corps comporte un remplissage de petits points (voir photo 6). Le zoomorphe est localisé dans une niche très bien individualisée de la paroi de l'abri. La figuration correspond au numéro 2 et au panneau CCLXIX de l'inventaire.



Croquis 4 : Coupe stratigraphique du B.P.F.22

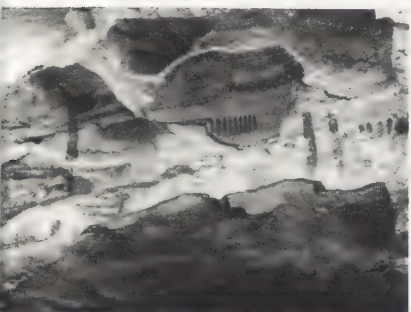


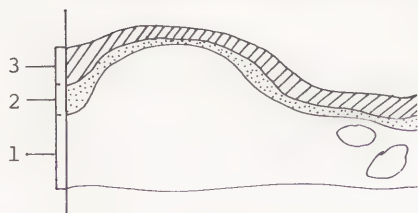
Photo 4 : Localisation du prélèvement B.P.F.23



Croquis 5 : Coupe stratigraphique du B.P.F.23



Photo 5 : Localisation du prélèvement B.P.F.47



Croquis 6 : Coupe stratigraphique du B.P.F.47

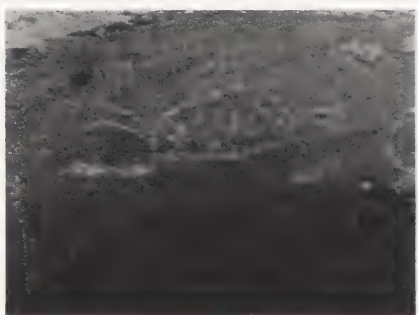
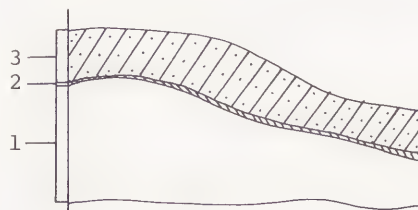


Photo 6 : Localisation du prélèvement B.P.F.43



Croquis 7 : Coupe stratigraphique du B.P.F.43

L'observation au microscope révèle (voir croquis 7) :

- une couche blanche (couche 1) avec les grains de quartz bien individualisés de la roche
- un très fin "liseré" blanc (couche 2, épaisse de 2 μ m environ)
- une couche grise (couche 3 d'épaisseur moyenne 56 μ m) composée de granulations minuscules (de dimensions de l'ordre de 2 à 3 μ m) rouge foncé d'ocre rouge entourées d'une matière blanc-grisâtre.

B.P.F. 19 :

Prélèvement de couleur dite "rouge clair" (réf. code Munsell 10R 6/8) fait sur une représentation zoomorphe de profil (nandou, voir photo 3) appartenant à un groupe de 3 animaux (numéro 14 du panneau CCXXXIII de l'inventaire). Le zoomorphe correspond à la technique d'exécution du contour complété d'un remplissage au trait. Les tracés paraissent avoir été effectués sur un dépôt superficiel blanc présent encore à côté des figurations pariétales sur la paroi nue.

A la loupe binoculaire, on remarque l'existence d'un épais dépôt blanc sous la couche pigmentaire.

Au microscope, l'étude stratigraphique (voir croquis 8) confirme ces remarques :

- une couche épaisse de dépôt blanc (couche 1), sans matérialisation de la forme des grains
- une couche discontinue et fine d'ocre rouge (couche 2 d'épaisseur moyenne 6 μ m).

B.P.F. 29 :

Prélèvement de couleur jaune (référence du code Munsell 10YR 7/8), fait dans le corps d'un anthropomorphe exécuté selon la technique du contour fermé sans remplissage dans le corps (voir photo 7). Il a le numéro 28 du panneau CCXXXIV de l'inventaire.

A la loupe binoculaire les pigments paraissent entourer les grains de quartz en saillies.

L'étude stratigraphique met en évidence (voir croquis 9) :

- une couche blanche (couche 1) formée des grains de quartz du grès
- une couche d'ocre jaune (couche 2 d'épaisseur 11 μ m)
- une couche blanchâtre (couche 3) correspondant à un dépôt superficiel (non visible sur le document).

B.P.F. 20 :

Prélèvement pris dans la partie en superposition d'un zoomorphe (nandou) de couleur jaune (référence Munsell 10YR 6/8) et un autre zoomorphe (nandou) de couleur rouge foncé (référence code Munsell 10R 4/8). La technique d'exécution de ces figurations est du type dessin avec contour fermé et remplissage lisse (voir photo 3). Elles correspondent aux numéros 6 et 6a du panneau CCXXXIV de l'inventaire. L'observation à la loupe binoculaire révèle une surface irrégulière avec de gros grains de quartz. Sont visibles la superposition du pigment rouge foncé sur le pigment jaune contrairement aux observations faites sur le terrain, ainsi que la présence d'un produit d'altération sous les pigments. Il ne nous est pas possible dans l'état de nos observations actuelles de fournir une explication de cette inversion, l'erreur d'interprétation en laboratoire étant exclue. Sur l'autre face du prélèvement de la roche on observe un dépôt blanc sous forme de petits cristaux et quelques points noirs.

L'étude stratigraphique permet de distinguer (voir croquis 10) :

- une couche blanchâtre (couche 1) avec des cristaux de quartz
- une couche jaune d'ocre jaune (couche 2)
- une couche rouge d'ocre rouge (couche 3, épaisseur 2 μ m).

3.2.2. Résultats d'analyses chimiques

Des résultats complémentaires ont été obtenus au microscope électronique à balayage et à la microsonde électronique associée pour l'échantillon B.P.F. 43. Au niveau de la "couche grise", décrite précédemment lors de l'étude stratigraphique, nous pouvons différencier des concentrations de fer localisées dans les granulations puis du silicium, de l'aluminium et du potassium dans la matière blanc grisâtre. Par diffractométrie de rayons X, nous avons pu pour ce même échantillon, distinguer quatre composants différents : quartz, kaolinite, illite et hématite. La matière blanc grisâtre est donc une argile.

Sur le site du Boqueirao do sitio da Pedra Furada, nous avons remarqué la présence fréquente de surfaces de dimensions variables couvertes d'efflorescences de couleur blanche, associées ou non aux parties décorées. L'analyse par spectrophotométrie infrarouge a révélé la présence de nitrate de calcium.

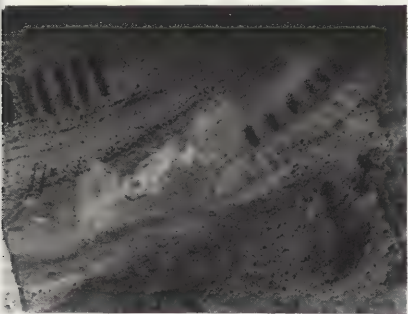
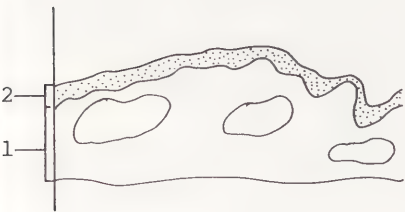
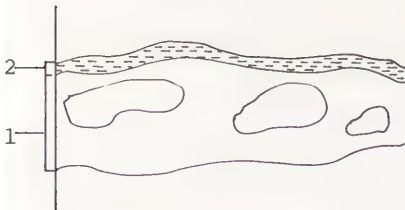


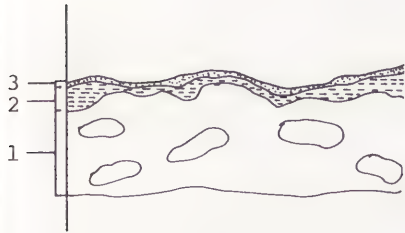
Photo 7 : Localisation du prélèvement B.P.F.29



Croquis 8 : Coupe stratigraphique du B.P.F.19



Croquis 9 : Coupe stratigraphique du B.P.F.29



Croquis 10 : Coupe stratigraphique du B.P.F.20

LEGENDES

- Dépôt blanc
- Pigment blanc
- Pigment jaune
- Pigment gris
- Pigment rouge

L'examen en laboratoire a montré aussi la présence de minces dépôts en surface des peintures (B.P.F. 11, B.P.F. 22, B.P.F. 42). Leur analyse par spectrophotométrie infrarouge révèle divers composants : sulfates, oxalates, nitrates en qualité et proportions variables selon les prélèvements.

L'analyse par fluorescence X de l'ensemble des prélèvements indique la présence de calcium et de fer en quantité importante (tableau I récapitulatif des analyses ci-après).

Eléments									
N° Echantillon		Ca	Fe	K	Si	Al	S	Ti	Zn
BPF 19	Air	X	X						
	Sous vide	X	X		X	T		T	
BPF 20	Air	X	X					T	
	Sous vide	X	X						
BPF 22	Air	X	X					T	
	Sous vide	X	X		T			T	
BPF 23	Air	X	X				T	T	T
	Sous vide								
BPF 29	Air	X	X						
	Sous vide	X	X				T		
BPF 35	Air	X	X						
	Sous vide	X	X						
BPF 38	Air	X	X				T		
	Sous vide	X	X				X		
BPF 43	Air	T	X	X	T		T	X	
	Sous vide		X	X	X	T	X	T	
BPF 47	Air	X	X		T		T		
	Sous vide	X	X	T			T	T	T

T = Traces
X = Présence

4 - Conclusions :

Les prélèvements de peintures de la Toca do Boqueirao do Sitio da Pedra Furada étudiés ont une stratigraphie picturale en général simple. Les pigments ont été appliqués directement sur le support, sans préparation apparente de celui-ci. Les couches pigmentaires sont d'épaisseur variable, continues ou discontinues, denses avec ponctuellement des concentrations de colorants (ex. B.P.F. 22) et recouvertes en général d'un mince dépôt d'altération lui aussi plus ou moins continu. Il est tentant de donner un schéma type de la répartition stratigraphique des couches picturales où nous pouvons différencier : la roche, la ou les couches pigmentaires, un dépôt superficiel.

L'examen du prélèvement B.P.F. 38 a permis de préciser les relations des deux tracés de couleurs différentes (blanc et rouge) remarqués sur le terrain. A la partie ventrale de la représentation animale, le tracé rouge paraît être antérieur à celui du blanc. Par contre l'observation d'une section polie du B.P.F. 39) effectuée sur la partie dorsale de la même figuration révèle une superposition inverse: le tracé blanc est cette fois antérieur au rouge. Chaque trait du double contour de la figuration rupestre ne paraît pas avoir été dessiné en une seule fois d'un seul tenant; il faut renoncer à l'hypothèse du tracé de cette figuration par une première application d'une couleur suivie d'une deuxième application d'une autre couleur.

L'étude stratigraphique du prélèvement B.P.F. 43 révèle une couche externe (qui apparaît grise à l'oeil nu) hétérogène, formée de granulations rouges de couleur très dense "emballées" dans une "pâte" blanc-gris. Deux réflexions peuvent venir sur l'origine de cette couche : soit application par l'homme d'une matière contenant naturellement ces deux composants, soit application par l'homme d'un mélange.

L'examen au microscope optique peut confirmer les observations de terrain. C'est le cas de la superposition couche pigmentaire blanche sur couche pigmentaire rouge du prélèvement B.P.F. 38, c'est aussi le cas de la section polie correspondant au B.P.F. 19 où la couche pigmentaire est un dépôt blanc. Il peut aussi révéler des superpositions inverses de ce qui avait pu être constaté à l'oeil nu sur place; la section polie B.P.F. 20 illustre cette situation avec la couche rouge sur la jaune.

L'analyse des dépôts présents sur les parois montre une grande complexité ; les parois sont le résultat de toute une série de paléo-évolutions qui les ont plus ou moins marquées et ont plus ou moins dû laisser des traces. Cette diversité n'entraîne pas des conditions de conservation uniformes et il faudrait dans un proche avenir connaître la répartition - sous forme cartographique - de ces différents sels qui peuvent être à l'origine de graves désordres au niveau des aires décorées.

Après cette recherche, nous voulons souligner l'importance de l'archéométrie au sein des études de l'art rupestre. A partir des méthodes physiques et chimiques d'analyses de pigments, nous pouvons fournir des données qui faciliteront le travail du spécialiste d'art rupestre, confronté à des thèmes de recherche, tels que la ségrégation des figures ou les techniques d'exécution.

Il nous est agréable de remercier ici :

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Bibliographie :

M.B. ARNAUD : "les sites préhistoriques de la région Sao Raimundo Nonato, au sud-est du PIAUI - Brésil. Localisation et répartition géographique". Diplôme de l'Ecole des Hautes Etudes en Sciences Sociales, 1982, PARIS, 255 p.

J. BRUNET, S. DEMAILLY et P. VIDAL : In "8th Triennial meeting/ICOM Committee for conservation : Comité de l'ICOM pour la conservation, SYDNEY, Australia, 6-11 september, 1987". p. 1141-1147, Bibliographie. Résumé en français.

N. GUIDON : "Art rupestre : une synthèse du procédé de recherche". Cahier d'Etudes Américanistes Interdisciplinaires N°1, EHESS et RCP 394 CNRS, 1982, PARIS, p 41-54.

N. GUIDON : "De l'opérationnalité des classements préliminaires". Cahier d'Etudes Américanistes Interdisciplinaires N°2, EHESS et RCP 394 CNRS, 1983, PARIS, p 1-22.

N. GUIDON : "L'art rupestre du sud-est du Piaui dans le contexte sud américain. Une première proposition concernant méthodes et terminologie". Thèse de Doctorat d'Etat, Université de Paris I, 1984, PARIS, 1184 p.

J. PELLERIN : "Missão geomorfológica em Sao Raimundo Nonato, sudeste do PIAUI". Cadernos de pesquisa, série antropologia II, N°3, Universidade Federal do PIAUI, 1983, Teresina, PIAUI, p. 201-225.

A.M. PESSIS : "Méthodes d'interprétation de l'art rupestre : analyses préliminaires par niveaux". Cahier d'Etudes Américanistes Interdisciplinaires N°2, EHESS et RCP 394 CNRS, 1983, PARIS, p. 201.225.

A.M. PESSIS : "Art rupestre préhistorique : premiers registres de la mise en scène". Thèse de Doctorat d'Etat, Université Paris X, NANTERRE, 1987, 3 volumes.

RESUME

Une mission franco-chilienne a procédé en 1988 à la première étude scientifique pluridisciplinaire d'un tunnel de laves orné par les peintres pascuans il y a plusieurs siècles. Les autorités culturelles chiliennes conscientes du danger que représentent l'afflux des visiteurs libres d'une part, et la proximité de la mer d'autre part, s'inquiètent de la bonne conservation de ces oeuvres. Les données acquises préfigurent un programme de synthèse destiné à établir un bilan « pétro-pathologique » du milieu, préalablement à toute estimation du degré de dégradation.

Mots clés

Ile de Pâques - Climat tropical - Caverne peinte - Laves - Bilan hydrogéologique - Conservation.

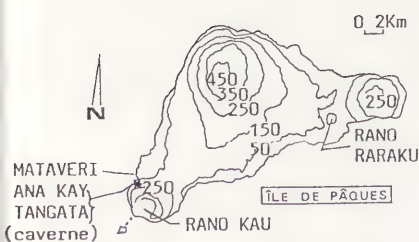


Fig. 1. Plan général de l'île.



Fig. 2. Plan de masse de la caverne.

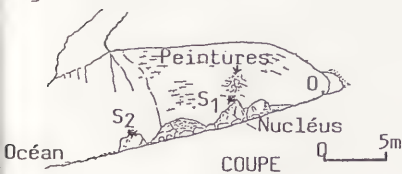


Fig. 3. Coupe verticale axiale Est-Ouest (topographie GERSRIP, 79, report: A. GAUTIER).

ETUDE CLIMATOLOGIQUE ET HYDROGEOLOGIQUE D'UN TUNNEL DE LAVES ORNE SOUS CLIMAT SUBTROPICAL. CAS DE LA CAVERNE PEINTE D'ANA KAY TANGATA (ILE DE PAQUES - CHILI)

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1. Introduction

Le Patrimoine Culturel de l'Ile de Pâques est surtout connu dans le monde entier par la présence de près de 900 statues (moais) dont la construction et le déplacement ont provoqué et provoquent encore autant de réflexions saines que d'élucubrations fantaisistes.

Il est un domaine moins connu mais extraordinairement passionnant, celui des peintures rupestres en tunnels où dans les maisons cérémoniales. Nous présentons ici une synthèse des résultats de la première mission scientifique franco-chilienne, orientée sur la détermination des causes de dégradation du milieu souterrain orné.

2. Situation et description

Ana Kay Tangata par sa situation au Sud-Ouest de l'Ile de Pâques (voir Fig.1), à proximité du village d'Hanga Roa et au pied de la falaise côtière de Mataveri, est très fréquentée par le public. C'est une grotte marine de faible longueur. Toutefois son porche imposant (8 mètres de haut et 17 mètres de large) lui confère un intérêt non négligeable parmi les cavités littorales de l'île. Les peintures qu'elle renferme constituent un attrait majeur; elles sont un témoignage historique de la civilisation pascuane et doivent être protégées et conservées dans les meilleures conditions possibles.

En général, l'archipel typique dans l'Océan Pacifique est protégé par des barrières de corail qui s'opposent considérablement à la genèse de ces creusements d'origine marine. Ce n'est pas le cas de l'Ile de Pâques dont toute la ceinture est directement soumise au déferlement des vagues de l'Océan. En outre, l'érosion régressive des falaises a recoupé les tunnels de lave dont on peut voir aujourd'hui les conduits ouverts à différentes altitudes.

Orientée approximativement Est-Ouest (du fond vers l'entrée-voir Fig.2), Ana Kay Tangata bénéficie d'un ensoleillement maximum à partir de la seconde moitié de la journée jusqu'à la période du soleil couchant. Les éboulis et sédiments qui encombrant l'entrée constituent la grève littorale. Dans sa longueur axiale elle se développe sur 20 mètres de façon fortement décline (entrée 0, fond +5 m-voir Fig.3). La totalité du sol est constituée d'alluvions, de blocs de charriage dans la partie la plus méridionale de la caverne.

Dans cette zone, très abondamment et finement délitée, se situent en parties basses vers l'Est et le Sud, des éboulis terminaux en connexion possible avec des prolongements occultes; toutefois, ces développements éventuels sont actuellement très colmatés. Dans les mêmes conditions, un conduit hypothétique se trouve au pied de la paroi septentrionale.

3. Morphologie et interprétation de la partie peinte

C'est dans la seconde moitié de la caverne par rapport à l'axe longitudinal, en partie haute de la paroi gauche, que se situent les peintures d'Ana Kay Tangata (voir Fig.2 et 4). Leur positionnement, aux deux-tiers de l'entrée vers le fond de la cavité, ne les protège peut-être pas de l'influence marine (le niveau de l'eau arriverait parfois à recouvrir la quasi-totalité du sol jusque sous les peintures). Les 9 figurations réparties sur une aire de 3,50 mètres de hauteur par 4,00 mètres de largeur, représentent essentiellement des oiseaux peints en rouge et blanc dont la signification est probablement liée au culte de Tangata Manu (l'homme oiseau).

Cette paroi Sud de la grotte et son prolongement en demi-voûte possèdent une homogénéité supérieure à la partie déjà décrite. Le litage ténu est ici moins présent bien que cette zone contenant les peintures soit assez délitée.

L'étude sur place de la paroi et l'analyse photo-interprétative des couples stéréoscopiques montrent que l'écaillage de la partie peinte s'effectue au bénéfice d'un plan de clivage sensiblement parallèle à la surface visible du support.

Cette altération se manifeste par des chutes de plaquettes fines aux faces irrégulières. Les causes sont d'ordre naturel (par effets mécaniques et hydrogéologiques) ou anthropique (chocs de pierres). Il est vraisemblable que ces mêmes phénomènes ont facilité la destruction complète d'une partie peinte située plus profondément.

4. Géologie

La caverne d'Ana Kay Tangata correspond à un tunnel de laves formé à la suite d'écoulements visqueux provenant d'une coulée émise à partir du cône du volcan Ranokau (voir Fig.1). Les laves basaltiques qui constituent l'enveloppe du tunnel ont une géométrie simple et concave pour la partie interne. Cette géométrie est par contre très complexe à proximité de la surface (voir photo n° 1). Ce sont des dalles horizontales puis redressées, plissées avec points de rebroussement qui forment des saillies au sommet de l'accumulation.

Description lithologique de la paroi peinte :

La paroi ornée se compose de dalles de basalte gris-noir, d'épaisseur variable (entre 5 et 40 cm). Leur morphologie est complexe et révèle l'hétérogénéité des phénomènes de détente mécanique liés aux contraintes qui s'exercent dans le milieu. Sous le panneau peint, on peut noter la présence d'un gros bloc de lave scoriacée non stratifiée (nucléus - Fig.3).

Les dalles se délittent en lames minces de 3 à 5 cm d'épaisseur. Les plans de décollement sont jointifs et seul le dernier est plus ou moins ouvert (de l'ordre du mm). Les surfaces internes et externes des dalles affleurantes sont recouvertes par une mince couche d'altération rougeâtre ou marron.

5. Climatologie aérienne

La climatologie aérienne sous toutes les latitudes joue un rôle capital quant à la répartition spatiale et temporelle des températures, de la pluie et des écoulements aériens et souterrains.

Ces éléments auront un impact différé sur le milieu souterrain et conditionneront la climatologie et l'hydrogéologie souterraines.

Nous avons donc suivi le maximum d'événements le jour comme la nuit afin de pouvoir comprendre et interpréter certaines données.

L'Ile de Pâques est soumise au climat sub-tropical humide de type océanique. Les températures sont peu contrastées entre les saisons extrêmes (20 à 24°C entre Novembre et Mai, 18 à 20°C, entre Juin et Octobre [1]).

L'altitude et l'exposition jouent un rôle primordial quant à la répartition des pluies. Les précipitations annuelles varient entre 1100 mm (zones côtières) et 1500 mm (zones élevées). Les mois les plus pluvieux sont ceux d'Avril, Mai et Août. Le mois le plus sec est celui de Novembre.

Durant toute la mission, nous avons noté une succession de journées nuageuses avec passages pluvieux intenses, mais de courte durée. Les séquences nuageuses étaient séparées par des phases d'ensoleillement plus ou moins longues soumises au rythme du vent fort, quasi permanent, en phase diurne.

6. Climatologie du tunnel

Des mesures rapprochées de la température et de l'hygrométrie de l'air ont été faites la nuit et le jour afin de pouvoir suivre et comparer l'évolution des valeurs absolues et les amplitudes des deux paramètres, ainsi que les échanges entre l'intérieur et l'extérieur de la caverne.

Les phénomènes majeurs à retenir sont les suivants :

6.1. Température de l'air

L'air de la grotte subit avec un léger retard et de façon atténuée les influences thermiques diurnes sous l'influence de la ventilation aérienne externe (voir Fig.5).

La grotte constitue une cellule thermique indépendante de l'extérieur en phase nocturne lorsque le vent est faible à nul (voir Fig. 5a).

La grotte conserve une capacité calorifique nocturne supérieure à celle de l'extérieur même avec un vent moyen.

Cette situation est très importante car elle assure une fluctuation atténuée des différences de température entre l'intérieur et l'extérieur d'une part, entre le jour et la nuit d'autre part.

6.2. Hygrométrie de l'air

Quant aux variations hygrométriques de l'air, le tracé des courbes montre bien que les gradients sont généralement plus faibles à l'intérieur qu'à l'extérieur en période ventilée diurne.

Inversement, en phase nocturne le "mur thermique" permet l'accroissement rapide du degré hygrométrique de l'air de la cavité (cf. le 27/2 entre 0 h et 02 h) par emprunt sur les parties humides des parois (cf. paragraphe "Hydrogéologie" n° 8 ci-après).

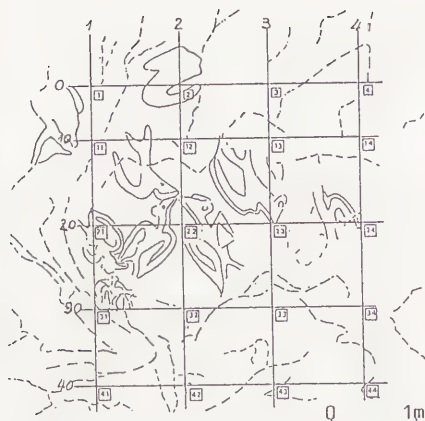


Fig. 4. Surface rocheuse ornée et grille des mesures.

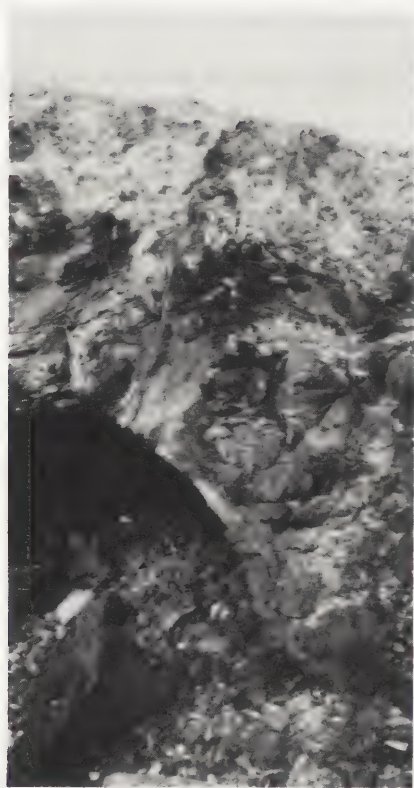


Photo n° 1 - Vue générale sur l'entrée de la caverne et sur la disposition des dalles de lave.

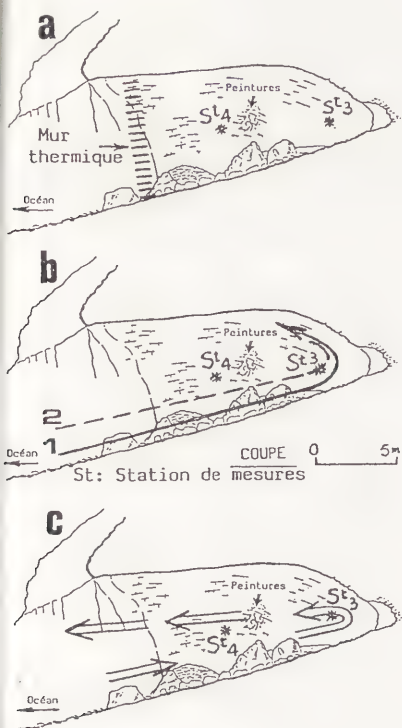


Fig. 5. Ventilation de la caverne.

- a) - pas de vent, mer calme
- b) - vent faible, mer calme
- c) - vent moyen, mer agitée.
- 1= courant d'air au sol
- 2= courant d'air à 2m au-dessus du sol.

En définitive et pour faire le point de la climatologie valable pour la période d'étude, nous écrirons que la cavité constitue naturellement un milieu tamponné tant du point de vue thermique qu'hydrique. Les calories sont conservées par la mise en place, la nuit, d'une cellule indépendante de l'extérieur.

L'éventuel déficit hydrique de la journée est compensé la nuit par évaporation d'eau de suintement (cf. paragraphe 8 ci-après) principalement à partir des surfaces humides du fond de la grotte.

7. Thermomécanique

La connaissance de la dynamique évolutive de la paroi rocheuse peut nous renseigner sur la prédisposition pariétale à l'écaillage.

Ce chapitre est donc très important dans le sens de l'interprétation de l'équilibre mécanique présent et futur de la paroi ornée et du site souterrain.

Différents paramètres entrent en jeu dans ce phénomène. Il y a eu tout d'abord dans un passé lointain la mise en place des matériaux sous fortes pressions soit mécaniques, soit de l'environnement marin, puis l'identification après refroidissement d'une structure en dalles (basalte) avec présence de noyaux amygdalaires de lave bulleuse; il y a enfin la couleur du matériel géologique. On sait en effet que les roches éruptives de couleur sombre (andésites, amphibolites, basaltes etc...) ont une capacité d'absorption calorifique bien supérieure à celle des roches de couleur claire.

Dans cette recherche, nous avons construit 5 cartes d'isothermes à des temps différents puis nous avons dessiné une carte de synthèse.

L'analyse de ce document (voir Fig.6) nous permet d'établir un premier bilan de l'état thermique de surface (T.S.) valable uniquement pour la période considérée.

La partie ornée de la paroi est intégrée dans une gamme de T.S. évolutives mais homogènes, caractérisées par une faible différence ($\Delta T.S.$) pour un instant donné. Les écarts absolus restent du même ordre de grandeur hormis une petite surface proche de la base du dessin F1 et une autre associée au nucléus (voir Fig. 3).

Dans le détail, la grotte est soumise à l'action journalière du soleil mais de façon atténuée. Les effets diurnes sont effacés dans les quelques heures (3 à 5) qui suivent le coucher du soleil. L'influence des ondes saisonnières se fait sentir sur toute la paroi peinte et elle provoque de ce fait la diminution des écarts de T.S. entre le jour et la nuit d'une part, entre les extrêmes d'autre part. L'influence du flux géothermique a pu être mise en évidence à la base de la caverne.

8. Hydrogéologie

8.1. Inventaire des différents types d'eau

Un premier examen des lieux nous a permis de constater la multiplicité des phénomènes faisant intervenir l'eau en phase liquide et vapeur.

Dans l'ordre de leur découverte et en ne leur attribuant qu'une valeur relative nous citerons :

- l'eau de ruissellement :

Les pluies violentes des jours qui précéderent notre arrivée avaient provoqué de forts ruissellements le long du chemin menant à la grotte, aux alentours immédiats de cette grotte et à la voûte sur le porche.

- l'eau d'infiltration :

Nous avons observé des zones (en particulier à la voûte, au fond de la grotte) où l'eau d'infiltration émergeait entre deux fissures et tombait sur le sol.

- l'eau d'évaporation :

L'eau qui humidifiait certaines parties de la roche s'évaporait rapidement en liaison avec un déficit notable du degré hygrométrique de l'air de la caverne.

- l'eau sous forme d'aérosols marins (embruns) :

La grotte est séparée de la mer par une plage faite de blocs rocheux et de galets.

Les vagues en se brisant sur les rochers créent une écume abondante. Lorsque le vent souffle, cette écume est transformée en aérosol. Celui-ci est transporté vers la falaise et peut pénétrer, en partie, à l'intérieur de la grotte.

Du 26/02/88 à 6 H au 27/02/88 à 12 H

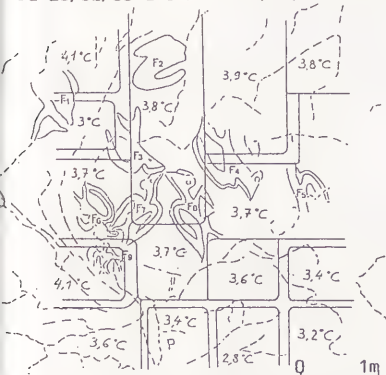


Fig. 6. Carte des amplitudes thermiques maximales de la surface rocheuse peinte ($\Delta t=30$ H).

L'eau de ruissellement :

Elle présente un certain danger pour la conservation du milieu en raison de fortes pentes du terrain et de la présence de gros blocs en équilibre instable.

L'eau d'infiltration :

La caverne est creusée dans le substratum rocheux constitué de laves basaltiques empilées les unes sur les autres sur une vingtaine de mètres d'épaisseur. Ces laves sont couvertes par une couche d'altération discontinue, argilo-sableuse et micacée. (c.a.). Cette couche est surmontée par un sol recouvert d'herbes (horizon pédologique h.p.). Les niveaux h.p. et c.a., sont poreux perméables et laissent passer une partie de l'eau d'infiltration.

Cette eau pénètre dans les fissures et les joints ouverts entre les dalles de laves et arrive à la surface des parois de la caverne avec un retard plus ou moins grand par rapport à la phase de pluie initiale. Elle s'évapore rapidement comme nous l'ont montré les mesures effectuées à l'évaporomètre et elle maintient un degré hygrométrique élevé dans l'air.

Cette humidité est importante pour éviter la dessiccation de l'air, de la surface des parois rocheuses et des surfaces peintes. Elle assure la cohésion des pigments entre eux et sur la roche.

L'humidité pariétale a fait l'objet de mesures régulières et les résultats obtenus nous ont permis de construire des cartes évolutives avec un décalage de 6 heures (cf. Fig. 7).

8.2. Interprétation cartographique

Sur une durée de 30 heures et pour des conditions climatiques assez contrastées, on remarque que l'humidité superficielle de l'ensemble de la zone peinte reste homogène.

Seule la dalle esquilleuse, de couleur gris cendré sur laquelle est peinte la figuration F4 et les dalles gris-bleues situées à droite de F2 révèlent une très légère perte d'eau à 18 heures le 26/02/88 pour la première, et à 12 heures le 27, pour la seconde.

L'analyse détaillée des mesures révèle en outre la localisation de micro-venues d'eau en A1, A2 et A3.

Ces trois plages alimentées régulièrement ont été envahies par les micro-organismes.

8.3. Les aérosols marins (embruns)

La dynamique des embruns a été suivie par journée de grand vent et forte mer propice au déferlement des vagues sur les rochers.

Le contrôle nous a permis d'identifier certaines zones où l'impact des embruns était net et d'autres où les dépôts sont absents, en particulier au droit de la zone peinte. Ce premier résultat n'est pas définitif; il devra être confirmé par d'autres mesures.

9. Bilan des premiers résultats obtenus

Après une mission correspondant à une phase climatique caractéristique de l'Ile de Pâques, il est évident que nous ne pouvons pas parler de conclusion. Néanmoins des tendances significatives apparaissent. Ces tendances sont basées sur des mesures. Elles excluent donc les sensations ou les sentiments personnels.

La caverne d'Ana Kay Tangata a donc été creusée dans des laves basaltiques. Ce tunnel est fermé au fond par un énorme éboulis fait de gros blocs de lave. Durant l'été la mer reste entre 27 et 30 mètres de distance du fond de la caverne, c'est à dire entre 19,50 et 21,50 mètres de distance des peintures. Son pouvoir d'érosion mécanique ne se manifeste qu'au niveau des blocs parsemés au bord de la crique. Le sol naturel va en descendant du fond de la caverne vers la mer. Cette morphologie est favorable pour faire obstacle aux vagues.

La paroi peinte est constituée de dalles dont la taille, la forme, la couleur varient à quelques mètres de distance.

Les peintres pascuans ont choisi, à notre avis, ce qui pouvait être la meilleure surface rocheuse disponible. Ce choix judicieux n'est pas une surprise pour nous. Nous avons de nombreux exemples en France, en Europe, au Sahara, en Amérique du Nord où nous avons constaté la même chose [2].

Cette paroi évolue du point de vue de la thermique journalière de façon homogène. Durant la nuit, les facteurs externes à la grotte comme le gradient géothermique et l'onde saisonnière viennent compenser les écarts dus à la journée.

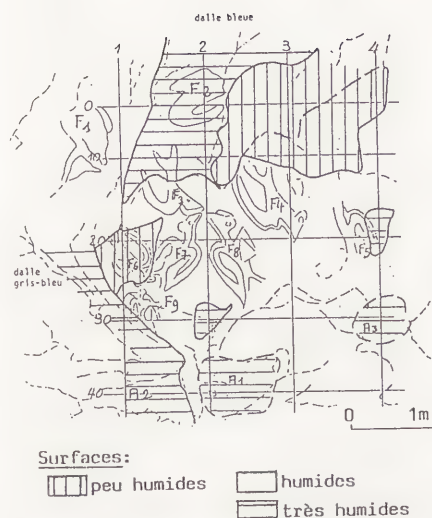


Fig. 7. Cartographie de l'humidité pariétale (27/02/88 à 12 H).

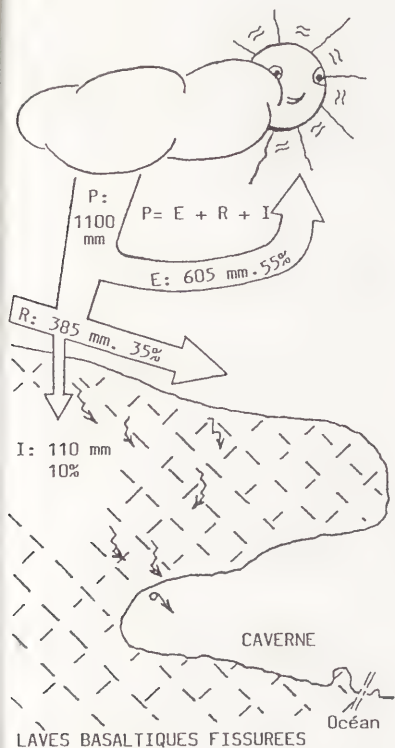


Fig. 8. Présentation des différents termes du bilan hydrologique de l'île.

P = pluie. E = évapotranspiration.
R = ruissellement. I = infiltration.

L'air qui entre dans la grotte a une hygrométrie qui fluctue au rythme des facteurs climatiques du jour et de la nuit. Durant notre mission, l'air extérieur est resté sous-saturé (valeur la plus basse mesurée : 67%) à l'exception des phases pluvieuses d'une durée de 0 h 15 à 3 heures durant lesquelles la saturation (100%) était atteinte. L'air intérieur est toujours resté sous-saturé (valeur maximale = 94% - valeur minimale = 70%).

Nous avons mesuré que l'air prenait de l'eau en permanence sur la roche. Cet état ne provoque pourtant pas la dessiccation de la surface rocheuse. La raison est connue. C'est l'eau d'infiltration qui a traversé le sol, puis les dalles basaltiques (circulation dans les fissures) et qui émerge dans les espaces entre les dalles en apportant la compensation hydrique permanente.

Cet apport par infiltration est faible comme le montre l'écriture du bilan hydrique obtenu par la mesure (P) et le calcul approché de l'évapotranspiration (E), en prenant pour la réserve en eau du sol une valeur de 110 mm (cf. Fig.8).

En ce qui concerne plus particulièrement le problème des aérosols marins, plusieurs séries de mesures rapprochées ont été faites pour des faciès climatiques et marins différents alors que les vagues étaient fortes et que le vent soufflait du Nord-Ouest vers le Sud-Est.

Ces mesures nous ont permis de comprendre le phénomène dans ses grandes lignes.

La morphologie de la caverne est telle que l'air chargé d'embruns qui pénètre à l'intérieur ne dépose pas les microgouttelettes d'eau de mer.

Le dépôt se fait à la verticale du porche et le long d'un surplomb extérieur de la paroi rocheuse, sur 9,50 m de longueur.

Pour achever ce premier bilan, nous écrirons donc que la situation climatique, morphologique, hydrique, hydrogéologique et hydrochimique de la grotte à peintures d'Ana Kay Tangata est actuellement bonne dans la mesure où les phénomènes naturels en saison chaude, se compensent de façon harmonieuse.

Des missions effectuées lors de phases saisonnières différentes conforteront ou moduleront ces résultats.

Remerciements :

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- Servicio de las Bibliotecas, Archivos y Museos.
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Bibliographie

- [1] - E.N.E. - Situación energética de Isla de Pascua - 1982 - Santiago - Chili
- [2] - J. Brunet - P. Vidal - J. Vouvé - Conservation de l'art rupestre. Unesco Paris - 1982 - Coll. " études et documents sur le Patrimoine Culturel "

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Working Group 25

Control of Biodeterioration

Contrôle de la biodétérioration



ABSTRACT

The Authors made clear in previous papers that xerophilic fungi are the main causes of foxing and that L-malic acid, glucose, cello-oligosaccharides and sixteen amino acids are deposited in foxed areas.

This paper reports in detail what combination of components kept in what environment can induce foxing. After L-malic acid, glucose, γ -aminobutyric acid, ornithine, aspartic acid, β -alanine, glycine and serine were spotted on hemp paper, these papers were incubated in relative humidity 75%, 84% and 94% at 25°C and 35°C for 30 to 40 days. It was discovered that characteristic components found in foxed areas, that is L-malic acid, glucose and γ -aminobutyric acid, are the main causes in the formation of foxing. The optimum environment for the induction of foxing is relative humidity 75% and temperature 35°C. This optimum environment coincides with the growth environment of xerophilic fungi.

KEYWORDS

foxing, browning reaction, xerophilic fungi, glucose, cello-oligosaccharides, γ -aminobutyric acid, amino acids, L-malic acid

INDUCED FOXING BY COMPONENTS FOUND IN FOXED AREAS

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INTRODUCTION

It has been reported in previous papers that foxed areas are composed of glucose and cello-oligosaccharides produced from cellulose of the paper and sixteen amino acids supplied by foxing-causing fungi (xerophilic fungi) (4,5). If cello-oligosaccharides and amino acids exist together in limited areas of foxing, a browning reaction may be accelerated between these components and browning materials may be made in foxed areas. The authors report in this paper the combinations of glucose and some amino acids that cause a browning reaction.

MATERIALS AND METHODS

Foxed areas are composed of organic acids, glucose, cello-oligosaccharides and amino acids. The authors experimented to see in what combination of these components a browning reaction appears.

(1) Components used

Saccharides:	Glucose
Organic acids:	L-malic acid, fumaric acid, lactic acid and gluconic acid.
Amino acids:	γ -aminobutyric acid, ornithine, aspartic acid, glutamic acid, β -alanine, glycine and serine.

(2) Inoculation and Incubation of Components

In the case of a single component test, one μ l of 0.01-10.0% of each solution was spotted on sterilized hemp paper (3 x 8 cm). In the case of combination tests of two components, after one μ l of the first component was spotted and dried, one μ l of the next component was spotted on the same position. The spotted hemp papers were dried, and then they were incubated in relative humidity (RH) 75%, 84% and 94% at 25°C and 35°C for 30 to 50 days.

(2.1) Test of single component

One μ l of each of the main components was spotted on sterilized hemp paper, that is 1.0% glucose solution, 0.13% L-malic acid solution, and 0.01-10.0% each of β -alanine, ornithine, aspartic acid, glutamic acid and serine.

(2.2) Combination tests of two components

After one μ l of 0.1-1.0% glucose solution was spotted on sterilized hemp paper, one μ l of 1.0-10.0% each of L-malic acid, fumaric acid, lactic acid and gluconic acid were spotted again on the top of the glucose solution. In the same way, after one μ l each of 0.1-1.0% glucose solution was spotted on hemp paper, one μ l each of 0.01-10.0% γ -aminobutyric acid, ornithine, aspartic acid, glutamic acid, β -alanine, glycine and serine were spotted again.

(3) Observation of browning reaction

After one μ l of foxing components were spotted on hemp paper and these papers were incubated in several environments, they were observed and pictures were taken under daylight and ultra violet light. Fluorescent pictures were taken by camera with UV protection filter (Nikon filter 52mm L39) under the irradiation of UV lamps (Toshiba FL20S BLB, 365nm).

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RESULTS

(1) Test of single component

Single spots of one μl of each component on hemp paper were incubated in RH 84% and 94% at 25°C and 35°C for 40 days. However, none of the spots of single component induced browning reaction on hemp paper.

(2) Combination tests of two components

(2.1) Glucose and organic acids

After combined spots of one μl of 1.0% glucose solution and one μl each of L-malic acid, fumaric acid, lactic acid and gluconic acid solution were made on hemp paper, these papers were incubated in RH 75%, 84% and 94% at 25°C and 35°C for 30 days.

As a result, a browning reaction could not be detected in any combination under daylight. However, when the same papers were observed under UV light, fluorescent materials were detected on those spots of glucose and L-malic acid, as well as on that of glucose and gluconic acid, which were kept in RH 75% at 35°C for 30 days and in RH 84% at 25°C and 35°C for 30 days.

(2.2) Glucose and amino acids

(2.2a) After one μl of 1.0% glucose solution and one μl of 0.1 and 1.0% β -alanine solution were spotted on the same position, these papers were incubated in RH 84% and 94% at 25°C for 40 days.

As a result, when a combination spot of 1.0% glucose and 1.0% β -alanine solutions was kept in RH 84%, a browning reaction of spot could be recognized under daylight. When the same spot was observed under UV light, the spot fluoresced clearly. However, we could not detect any browning phenomenon on the spot kept in RH 94%.

(2.2b) After combination spots of one μl each of 0.1, 0.5 and 1.0% glucose solution and 0.2% and 1.0% each of β -alanine, ornithine, aspartic acid, glycine, serine and glutamic acid solutions were made on hemp paper, these papers were incubated in RH 75%, 84% and 94% at 25°C and 35°C for 40-50 days.

As a result, when the combination spots of each concentration of glucose solution with 10.0% β -alanine, ornithine, glycine and serine solutions were kept in RH 75% and 84%, a browning reaction was induced clearly on these spots under daylight. A browning reaction of the same spots kept in RH 0.94 was not clear. When these spots were observed under UV light, they were clearly recognized by their fluorescence. When the induced conditions of brown spots are compared, the browning reaction of the combination spots had a tendency to appear more clearly under the conditions of RH 75% than 84%, a temperature of 35°C more than 25°C, concentrations of glucose solution 1.0% more than 0.5% than 0.1% and a concentration of amino acids of 10.0% more than 0.2%.

(2.2c) After combination spots of one μl of 1.0% glucose solution and one μl each of 1.0% and 5.0% β -alanine, ornithine, aspartic acid, γ -aminobutyric acid, glutamic acid, glycine and serine solutions were made on hemp paper, these papers were incubated in RH 75%, 84% and 94% at 25°C and 35°C for 40 days.

As a result, when the combination spots of one μl of 1.0% glucose solution and one μl each of 5.0% β -alanine, ornithine, γ -aminobutyric acid, glycine and serine solutions were kept in RH 75% and 84%, browning reactions were induced clearly even under daylight. However, the browning phenomenon was very difficult to recognize on these spots kept in RH 94%, and also the combination spots of one μl of 1.0% of the same amino acid solutions did not show clear brown spots.

Moreover, among amino acids that showed a browning reaction, the degree of foxing had a tendency to appear more with γ -aminobutyric acid than with glycine than with serine than with β -alanine and ornithine under daylight. Among these experiments, the optimum condition for induced foxing could be seen: namely, foxing appeared more in RH 75% than in 84%, at a temperature of 35°C more than at 25°C, and with a concentration of amino acids 5.0% more than with 1.0%. Since induced foxing on these hemp papers showed fluorescence, the formation of foxing was more easily detected by UV light observation than by daylight.

DISCUSSION

According to a series of experiments on foxing by the authors, the main causes of foxing can be considered to be xerophilic fungi (1,2,3). The authors propose the following as the formation mechanism of foxing. Airborne microorganisms and microdusts exist already on paintings and books. When these paintings and books are stored in an environment at 75-94% relative humidity and 25°C to 35°C temperature, conidia and ascospores of xerophilic fungi germinate and make their colonies of about 5 mm diameter around the microdusts. Growing fungi metabolize malic acid and other organic acids around their hyphae, and these organic acids deposit on fibers of the paper. The cellulose of the paper is attacked gradually and produces cellooligo-saccharides and glucose, after it has been in contact with malic acid and other organic acids for a long time.

The authors also reported previously that sixteen amino acids were found in foxed areas. Liquid chromatographic analysis of the foxed areas detected sixteen amino acids including γ -aminobutyric acid, aspartic acid, glutamic acid, ornithine, β -alanine, glycine, serine and others. Among them, the largest amount of amino acid found was γ -aminobutyric acid. This paper reports that induced foxing on paper was experimentally produced by the various combinations of glucose, L-malic acid and seven amino acids mentioned above. As a result, when the combination spots of one μ l of 1.0% glucose solution and one μ l each of 5.0% γ -aminobutyric acid, ornithine, β -alanine, glycine and serine solutions were incubated in RH 75% at 36°C for 30-40 days, browning reactions were detected clearly on paper even under daylight. Although browning reactions were induced in the environment of RH 84% at 25°C, it was not clear in RH 94%. It was known that when foxing caused by fungi is irradiated by a UV lamp of 365 nm, fluorescence can be seen. Since the hemp paper used for the experiments of induced foxing also show remarkable fluorescence, UV irradiation is a very effective way to check the initial stage of the formation of foxing.

CONCLUSION

Characteristic components found in foxed areas, L-malic acid, glucose and γ -aminobutyric acid, are the main causes in the formation of foxing. The optimum condition for induced foxing is an environment of RH 75% at 35°C. The authors consider that this optimum condition for the formation of foxing coincides with the preferred growth conditions for xerophilic fungi.

NOTES

1. H. Arai, "Microbiological Studies on the Conservation of Paper and Related Cultural Properties, (Part 1) Isolation of fungi from foxing on paper," Science for Conservation 23 (1984): 33-39.
2. H. Arai, "Microbiological Studies on the Conservation of Paper and Related Cultural Properties, (Part 5) Physiological and morphological characteristics of fungi isolated from foxing, foxing formation mechanisms and countermeasures," Science for Conservation 26 (1987): 43-52.
3. H. Arai, "On The Foxing-Causing Fungi (Microbiological Studies on the Conservation of Paper and Related Cultural Properties, Part 6)," in ICOM Committee for Conservation, 8th Triennial Meeting, Sydney (1987): 1165-1167.
4. H. Arai, N. Matsui, N. Matsumura and H. Murakita, "Biochemical Investigations on the Formation Mechanisms of Foxing, (Microbiological Studies on the Conservation of Paper and Related Cultural Properties, Part 7), 12th IIC-Kyoto Congress (1988); 11-12.
5. H. Arai, C. Nemoto, N. Matsui, N. Matsumura and H. Murakita, "Micro-biological Studies on the Conservation of Paper and Related Cultural properties, (Part 8) On the components found in foxing," Science for Conservation 28 (1989): 7-15.

ABSTRACT

The fumigant Vikane® (sulfuryl fluoride) was tested on a selection of materials, metals, pigments, resins, celluloses, proteins and dyes. Varying amounts of chemical and physical changes were noted in the materials, some of which could be attributed to the acidic impurities in the fumigant. Fumigations with the impurities removed from the Vikane® caused fewer changes. These results indicate that careful consideration of the fumigation conditions, pest type and materials to be fumigated must be taken into account.

KEYWORDS

Fumigant, Vikane®, sulfuryl fluoride, insecticide

LABORATORY INVESTIGATION OF THE FUMIGANT VIKANE®

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BACKGROUND

Insect infestation is a universal museum problem for which one must weigh the potential disadvantages of doing nothing, *versus* treating the infestation with a chemical agent. To do nothing runs the risk of severe damage to, even complete destruction of, the collection; to treat with a chemical agent runs the risk that it might interact with the objects being protected. There is usually no easy solution and the dilemma - to treat or not to treat - can be considerable.

Virtually all fumigants derive biological efficacy from their chemical reactivity. These agents then, unavoidably pose a risk to the types of materials found in museum collections. For this reason "integrated pest management" strategies which take into account various aspects of insect culture, good housekeeping, and low-level topical controls are always preferable to fumigations whenever possible. "Anoxant-type" fumigations which use nitrogen or another inert gas to virtually suffocate their target pest might, in the future, become the norm for museum insect control. For the time being, conditions sometimes exist which make traditional fumigation unavoidable and so it is necessary to identify which fumigants pose the least risks.

Some fumigants used in museums are summarized in Table I. Bell and Stanley[1] reported on a survey of curatorial practices in natural history museums in the United States and Canada. Most of the institutions were using space-type fumigants such as Dichlorvos (DDVP) or paradichlorobenzene (PDB). Dowfume 75 (30% carbon tetrachloride and 70% ethylene dichloride) was also commonly in use.

Table I. Some Fumigants Used in Museums and Their Effects on Materials

Fumigant	Effects
Carbon tetrachloride/ Ethylene dibromide (Dowfume 75)	Dissolves waxes, lacquers and rubber. Corrodes metals at high humidities.
Dichlorvos (Vapona)	Dissolves some resins, glues and plastics. Corrodes metals at high humidities.
Ethylene Oxide (Oxifume)	May cause premature aging of proteins. Leaves carcinogenic impurities in fats. Reacts with cellulose, resins and salts.
Methyl bromide	Forms disagreeable odor with sulfur-containing materials.
Phosphine (Phostoxin)	Corrodes copper, silver and gold. Reacts with ultramarine.
Sulfuryl fluoride (Vikane®)	Unknown. Liquid reacts with metals.

Unfortunately, the museum community is too small a market to interest most manufacturers in funding research on the possible effects of fumigants on collections. What little is published about potential damage is often the result of (a) the museum conservator or conservation scientist speculating on a fumigant's suitability from the chemical literature, or (b) the result of individual case histories where a fumigation for one reason or another has gone amiss or the product was misused.

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None of the fumigants listed in Table I can be called "ideal". Ethylene oxide (Oxifume) and carbon tetrachloride (in Dowfume) are carcinogenic; dichlorvos (Vapona) dissolves some organic substances and corrodes metals. Methyl bromide forms a disagreeable odor with sulfur-containing materials, including hair and feathers and phosphine corrodes copper, silver and gold. Fabrics which have been weighted or mordanted may also be susceptible to the fumigants which corrode metals (carbon tetrachloride/ethylene dibromide, dichlorvos and phosphine).

A measure of a fumigant's potential value to the museum community is the level of commercial consumer-related problems encountered. Vikane®, sulfuryl fluoride, has been shown to be satisfactory as a commercial fumigant when applied properly. Vikane® has been used to fumigate some historic structures and collections, such as the Hearst Castle in California, the Flagler Mansion in Florida and the Museum of the American Indian in New York. The United States, in which Vikane® is used for 50% of all domicile fumigations, and Japan are the only countries in which Vikane® is registered for use. A complete discussion of the chemistry and usage of Vikane® can be found in a literature review by the authors[2].

Because of the lack of problems encountered with Vikane® in domicile fumigations and its common recommendation by pest control experts for museum applications, the Getty Conservation Institute (GCI) sponsored a collaborative research project with the Canadian Conservation Institute (CCI) and the Conservation Analytical Laboratory (CAL) of the Smithsonian Institution to examine the effects of Vikane® on the materials found in objects of artistic, cultural or natural history value. CAL was responsible for assessing the effects on proteins and dyes; CCI, on cellulose and lignin; and GCI on natural and synthetic resins & polymers, waxes, pigments and metals (normally metals would not be the subject of fumigation but their presence as (a) metallic threads on tapestries, or (b) furniture fittings, especially gilded-brass mounts, makes them ubiquitous). Dow Chemical Company, which was responsible for carrying out all field fumigations, has been helpful and constantly open to suggestion during all phases of this work.

At the same time, Dr. Nan-Yao Su at the University of Florida was contracted by GCI to measure the efficacy of various doses of Vikane® on selected museum pests in the adult, larvae and egg stages[3]. This was thought an excellent opportunity to update the work on Vikane® efficacy as no mortality studies have been done, other than on termites, since Kenaga reported the first insect mortality studies with Vikane® in 1957[4]. Su's studies showed that higher doses than were previously recommended were necessary to kill 99% of the eggs of some of the pests studied.

This paper is a summary of the work done in this joint study from which certain general recommendations about fumigation with Vikane® can be made. Space does not permit a presentation of the materials, methods, data and results in detail; these can be found in the final reports[5,6,7], available from GCI.

CHEMISTRY OF VIKANE

The Dow Chemical Company patented the process for the production of sulfuryl fluoride (SO_2F_2) from an anhydrous gaseous mixture of sulfur dioxide, chlorine and hydrofluoric acid over a charcoal catalyst at 35°C. This process results in a product with a purity of greater than 99%. The remaining impurities in the commercial product are residual starting materials and by-products (HF , Cl_2 , HCl , SO_2) some of which are highly reactive and known to be a potential threat to acid-sensitive substrates. Vikane® is non-flammable. However, when exposed to high temperature (400°C), it decomposes to form hydrofluoric acid and sulfur dioxide. Thus a problem may occur if Vikane® reaches a heat source, such as a pilot light or electric heater element, and decomposes.

Vikane®, in its purest form, does not react with most materials. While it will hydrolyze in an alkaline medium, this hydrolysis is slow in neutral and acid solutions. Cady[8] found evidence for pH dependent, rapid reactions with some nucleophiles (NH_3 , $\text{C}_6\text{H}_5\text{O}^-$, CN^-), and Padma[9] et al. demonstrated that sulfuryl fluoride reacted with amines in solutions. Meikle[10] exposed graham flour to sulfuryl fluoride, labelled with S^{35} ; of the fumigant that was absorbed, almost all was found to be linked to the protein component of the flour.

An initial study by Dow[11] using radioisotopic labelling found that impurities in materials exposed to sulfuryl fluoride were considerably lower than those found in wood, cotton, paper, wool, nylon and other synthetic materials after exposure to methyl bromide. In fact, the only materials that showed any significant amount of impurities were moist proteinaceous food products. Retention of sulfuryl fluoride and its slow desorption has been suggested from a series of experiments by

Scheffrahn[12] et al. with typical household objects, especially for those made from polystyrene and polyester. The mechanisms for retention appeared to be physical in nature except for concrete where samples loaded with 8,000 ppm SO_2F_2 dropped to <10 ppb in 18 hours. Chemisorption or alkaline hydrolysis were suggested as routes for concrete's behavior as a Vikane® "sink".

EXPERIMENTAL

Prepared samples were shipped from Washington, D.C. and Ottawa, Canada to Los Angeles where, combined with the GCI samples, they were taken to the exposure site. The exposure chamber was a steel box of circa 28 m³ located at Dow's agricultural station near Davis, California (Sacramento). Three locations in the chamber were monitored for sulfuryl fluoride concentration in addition to humidity and temperature. From these concentration data, half-loss times (amount of time required for the concentration to drop to one-half of the initial concentration) could be determined.

Fumigations were performed on the samples in doses which fell between LD₉₅ for dermestid beetles (about 15 mg/l) and LD₉₅ for powderpost beetle eggs (about 36 mg/l). LD₉₅ represents the dose needed to kill 95% of a sample population. The variation in the doses resulted from changes in the sealability of the chamber, volume of samples and atmospheric conditions. Chloropicrin, an optional odorous indicator gas (sulfuryl fluoride has no odor of its own), was not used for these fumigations. Four fumigations were performed on separate sets of the materials to be tested; one of those fumigations was done using an experimental grade Vikane® from which the acidic impurities had been removed, and the rest were done using standard commercial grade Vikane®.

Cellulose and Lignin

Paper samples included rag papers from the 17th, 18th, 19th and 20th centuries, as well as modern newsprint and a modern buffered woodpulp paper. One of the 19th century papers samples was deacidified, to be compared with the modern buffered paper. Textiles included cotton and linen judged to be from the 18th century or older, cotton and linen from the 19th century, modern cotton and linen, and modern bleached jute.

The cold extracted pH of the paper samples was determined according to Tappi method T509 SU-68 "Hydrogen Ion Concentration (pH) of Paper Extracts - Cold Extraction Method". Fluoride content was monitored using a fluorine-selective electrode. Alkaline reserve (buffering capacity) of the buffered paper and deacidified paper was measured using a back titration procedure[13]. Carbonyl content was determined by nitrophenylhydrazine derivatization. Viscosity measurements of the samples dissolved in Cadoxen were performed to obtain the degree of polymerization (DP). Percent reflectance was measured at 416 nm, using an integrating sphere, to monitor brightening or darkening. Portions of the samples were artificially aged at 70°C and 50% R.H.

Proteins and Dyes

Protein samples included leathers (chrome-, oak- and untanned), photographic gelatin, hide glue, albumin, casein, silk and wool. Dyes (on wool) included madder, cochineal, weld, indigo, Orange II, Ponceau RR, Naphthol Yellow, Magenta Fuchsin and Victoria Blue B.

Amino acid analysis (AAA) on the proteins was performed by High-pressure Liquid Chromatography (HPLC) using the Waters PICO-TAG system. The pH of the proteins was monitored using a surface pH electrode. Color changes in the proteins and the dyed wool yarns were measured between 400 and 700 nm, using an integrating sphere. Extraction tests were carried out on the dyed wools and thin-layer chromatography (TLC) performed on the extracts. Portions of the protein samples were aged at 90°C and 50% R.H. and portions of the dyed textiles were faded in an Atlas Weather-ometer.

Resins, Waxes, Pigments and Metals

The resins tested include the major natural (such as dammar, mastic and shellac) and synthetic (such as Acryloid B-72 and Incralac) resins. Other synthetic polymers included AYAA (polyvinyl acetate) and Araldite GY 502(an epoxy). Microcrystalline, Carnauba and beeswax, as well as gum arabic and linseed oil were included. The metals tested were copper, lead, silver, tin, steel, brass and bronze, and the

pigments were lead white, ultramarine, malachite, azurite, and calcium carbonate. Some metals were tested after coating with resins or anti-tarnishing agents, such as BTA.

The resins, oil, gum and waxes were analyzed by Fourier-Transform Infrared Spectroscopy (FTIR). The pigments were monitored by x-ray diffraction (XRD) and color changes measured by visible spectrophotometry. Changes in the surface of the metals were monitored by visual inspection and Electron Scanning Chemical Analysis (ESCA)/Auger.

RESULTS AND DISCUSSION

Cellulose and lignin

The results are summarized in Table II. The complete data and discussion of results are available in the final report on the project[5]. The extracted pH of the samples fumigated with commercial grade Vikane® decreased by 0.1 pH unit, indicating an increase in acidity. The increase in acidity could be due in part to the acidic impurities in the commercial grade fumigant. The alkaline reserve (buffering capacity) of the modern buffered paper did not change significantly after fumigation, whereas the buffering capacity of the 19th century paper deacidified by standard techniques decreased. This indicates that, while buffering may afford a paper some protection from the acidic impurities in the commercial grade fumigant, there is still some reaction between the fumigant and an aged paper which will produce an increase in acidity.

After fumigation, the carbonyl content of some naturally aged papers decreased; the carbonyl content of some modern papers increased after accelerated ageing (70°C, 50% R.H.). Increased carbonyl content is usually an indication of increased oxidation. Papers containing lignin showed an increase in carbonyl for both cellulose and lignin fractions. For the textiles very little change in the carbonyl content was observed after fumigation (the textiles are composed mostly of pure cellulose, of higher degree of polymerization (DP) than the processed cellulose in paper).

Table II. Results of Fumigation Studies on Cellulose and Lignin (CCI)		
Property	Result	
	Commercial Grade Vikane®*	Experimental Grade Vikane®**
cold extracted pH	decrease of 0.1 pH units	less decrease
alkaline reserve	decrease	less decrease
carbonyl content	naturally aged papers decrease; modern papers increase after accelerated aging; papers containing lignin show increase for cellulose and lignin fractions; textiles show little change	less change after aging
degree of polymerization (cellulose)	decrease for aged, unbuffered, low MW papers	less decrease
fluoride content	increase for gelatin sized papers, unaged alkaline papers and textiles	less increase
color	all samples brighten (detectable by instrument only)	less change
* 25 paper and textile samples tested		
**Acid impurities removed from fumigant; 2 papers only tested		

A large decrease in the average DP of the cellulose between non-fumigated and fumigated samples was observed for four out of eight paper samples after accelerated ageing. Papers showing little change were either buffered (presumably protected from acidic attack) or the cellulose had a DP near the micro-crystalline level (DP of 200-250) before fumigation. As this DP value is on the lower limits of the method's ability to measure, a small change in DP would not be detected.

The fluoride content was elevated in unaged paper samples which had gelatin-sizing or were alkaline and in alkaline textiles. The increased fluoride content suggests that the fumigant (or its impurities, such as HF) are reacting with the cellulose and binding to it.

Color changes after fumigation were not perceptible to the eye, but instrumental methods indicated brightening. This could be caused by a reaction with the acidic impurities, by destruction of chromophores.

Two late 19th century ledger papers (one alkaline) were fumigated with an the experimental grade Vikane®. Results show that the magnitude of changes seen with the experimental grade Vikane® are less than with the commercial grade fumigant. This indicates that while some change is probably being caused by the sulfuryl fluoride itself, a significant portion may be due to the acidic impurities present in the commercial Vikane®.

Increased acidity, oxidation and decreased DP are considered to be undesirable in cellulose and are eventually manifested as an increased rate of degradation, yellowing and loss of strength. While the amounts of changes seen here are not great, they do indicate that fumigation of cellulosic materials with sulfuryl fluoride should not be considered a trivial matter.

Proteins and Dyes

The results are summarized in Table III. The complete data and discussion of results are available in the final report on the project[6]. Fumigation with commercial grade Vikane® demonstrated only two effects in the protein samples: a reduction in pH and color changes; the color changes being manifested as an initial lightening with darkening during subsequent artificial aging of the fumigated materials. Although these color changes were statistically significant, they were not large enough to be considered detectable by the human eye.

Table III. Results of Fumigation Experiments on Proteins and Dyes (CAL)			
Property		Result	
		Commercial Grade Vikane®	Experimental Grade Vikane®*
Proteins	Amino Acid Analysis (AAA)	no change	no change
	surface pH	decrease	no change
	color	lightened (detectable only by instrument)	no change
Dyes	color	not fumigated	no change
	extractions	not fumigated	no change
	Thin Layer Chromatography (TLC)	not fumigated	some changes
*Acid impurities removed from fumigant			

Amino acid analysis showed no changes in the content of the proteins after fumigation and after artificial aging. This indicates that there were no measurable amounts of amino acids being destroyed by the fumigation.

No measurable color differences were detected in the dyed yarns. As the yarns were wrapped by hand around cards for measuring, the standard deviations of the data were larger than that of the proteins, but still below the level which can be detected by eye.

The fumigated and unfumigated dyed wool yarns performed identically in extraction tests; however, the thin layer chromatograms of fumigated and unfumigated dyes were different for some synthetic and natural dyes. In some cases, some spots present in the unfumigated dye TLC's were not observed in the fumigated dye TLC's. In other cases, differences in elution times were seen. These extraction and TLC tests are often relied upon to identify the dyes used in textiles; changes in their results would cause the tests to be less useful for identification of fumigated

dyed textiles. The changes in the TLC's indicates a chemical reaction which, while causing no measurable color difference, changed the polarity of some of the dye molecules.

No changes were detected in proteins when fumigated with the experimental grade Vikane®, which suggests acid impurities in the commercial grade Vikane® as the most likely causative agent of the color and pH changes.

The slightly increased acidity in the proteins is not as threatening to the materials as it is in cellulose, as proteins are less affected by an acid environment. It appears that even that slight change can be avoided by removal of the acidic impurities in the fumigant before use. The changes seen in the TLC's of the dyes, however, are more of a problem as they will inhibit characterization of the textile. It may be that repeated fumigation would change the polarity of the dye enough to change its fastness in certain solvents.

Resins, Waxes, Pigments and Metals

The results are summarized in Table IV. The complete data and discussion of results are available in the final report on the project[7]. In spite of sample

Table IV. Results of Fumigation Studies on Resins, Polymers, Waxes, Pigments and Metals (GCI)			
Property		Result	
		Commercial Grade Vikane®	Experimental Grade Vikane®*
Resins, polymers and waxes	Fourier-Transform Infrared (FTIR) spectrum	no change (except epoxy and linseed oil, after aging, and polyvinyl acetate)	not done
Pigments	X-Ray Diffraction (XRD)	no change	not done
	color	not done	no change
Metals	visual inspection	some corrosion	no change
	Electron Scanning Chemical Analysis/Auger (ESCA/Auger)	sulfur layer with trace of chlorine	not done
*Acid impurities removed from fumigant			

preparation that presented the largest surface area per weight of material, no significant changes were detected in the FTIR spectra of most of the organic materials. The spectrum of the polyvinyl acetate (AYAA) sample had increased absorbances in the regions where fluorine compounds typically absorb. Newly fumigated linseed oil had no difference between the spectrum of the fumigated and unfumigated samples, but after three years in a dark drawer, a small change was seen in the form of a new peak in the region where the C=O bond of esters and carboxylic acids absorb. In addition, a major change was found as well between the infrared spectra of the fumigated and control epoxy (Araldite) in the form of an increased amount of absorbance in the region where the C-O bond of esters absorbs.

No differences were detected in the x-ray diffraction patterns of the fumigated and unfumigated pigments. Color measurements showed no measurable changes in the colors of the pigments which could be related to the effects of the fumigant.

Surface analysis of the metals varied slightly with alloy but generally indicated a layer from 200-300 angstroms thick rich in sulfur and with traces of chlorine. Binding energies for sulfur on copper indicated a sulfide; however, the brass sample suggested, in addition, that some sulfur was in a higher oxidation state, probably as zinc sulfate. Corrosion was visible by eye on some of the samples. Metal coupons coated with anti-tarnishing agents or resins experienced less tarnishing after exposure to the commercial grade Vikane® than untreated metals.

The metals exposed to the experimental grade Vikane® did not exhibit visible levels of corrosion. As with the other materials, this suggests that the changes seen with the commercial grade fumigant are due in part or whole to the acidic impurities.

The results suggest that Vikane® does not have an immediate measurable effect on the pigments, resins, and waxes studied. The changes seen in the infrared spectra of the polyvinyl acetate, linseed oil and epoxy suggest that sulfuryl fluoride or its acidic impurities reacts with some materials and, in the case of the linseed oil and epoxy, causes a change in their aging characteristics. The corrosion seen in the metals may be due to the acidic impurities in the commercial fumigant. It appears that the effect can be reduced by treating the metals with BTA or coating with a resin before fumigation, but it seems safer to exclude the acidic impurities where possible. Metals, as such, would not need to be fumigated, but may be contained as part of an object which requires fumigation.

CONCLUSIONS

Evidence was found of the potential for damage as a result of fumigation by Vikane®; the experimental grade caused less damage in some cases than the commercial grade, which suggests the acidic impurities in commercial grade Vikane® as the cause of some of the damage. However, changes were still seen in cellulosic materials and dyes after fumigation with the experimental grade, which indicates a reaction with the sulfuryl fluoride itself. In addition, there could be long-term effects which were not measurable in these studies.

The danger in any fumigation study is that it may be used either as an excuse never to fumigate or as justification for repeated "routine" fumigations. No collection should be subjected to repeated fumigations if the infestations can be prevented by attention to housekeeping nor should pieces be fumigated in which no infestation can be identified. However, where housekeeping has failed and the infestation can not be handled by non-chemical methods, fumigation of some sort should be considered. It can not be emphasized enough that the worst damage seen in these studies is still far less than that done by an uncontrolled infestation. Those considering fumigation with Vikane® should consult the results presented in detail in the final reports in this study[5,6,7] to decide whether the potential damage to the objects is justified.

The results seem to indicate that removing the acidic impurities from Vikane® may result in less potential for harm to the materials fumigated. It certainly makes sense to avoid exposing the materials to acids where possible. It is presently unknown whether the experimental grade used here will ever be commercially available; however, it may be possible to remove the acidic impurities from commercial grade Vikane® immediately before fumigation by way of a gas filter.

There are some obvious directions for future work on the effects of Vikane® on materials. Since it appears from Su's studies that higher doses are necessary to kill the eggs of certain museum pests than previously recommended, further fumigation studies should include the effects of higher doses. One way to avoid the high doses would be to perform two fumigations, the first killing the adult pests, and the second, performed after the surviving eggs would hatch, to kill the larvae from those eggs. Therefore, studies which compared the effects of multiple low-dose fumigations *versus* one large dose would also be useful.

NOTES

1. Bell, Bruce M. and Edith M. Stanley, "Survey of Pest Control Procedures in Museums", in Pest Control in Museums: A Status Report (1980), Stephen R. Edwards, Bruce M. Bell and Mary Elizabeth King (eds.), Association of Systematics Collections, Lawrence, KS, 1981.
2. Derrick, Michele R., Helen D. Burgess, Nancy E. Binnie and Mary T. Baker, "Sulfuryl Fluoride (Vikane®): A Review of Its Uses as a Fumigant", accepted for publication in Journal of the American Institute for Conservation.
3. Su, Nan-Yao, "Efficacy of Sulfuryl Fluoride Against Four Beetle Pests of Museums (Coleoptera: Dermestidae, Anobiidae)", Journal of Economic Entomology, in press.
4. Kenaga, E. E., "Some Biological, Chemical and Physical Properties of Sulfuryl Fluoride as an Insecticidal Fumigant", Journal of Economic Entomology, vol. 50, no. 1, (1957) pp. 1-6.
5. Burgess, Helen D., and Binnie, Nancy, "Potential of Adverse Effects of Pest Control Agents on the Materials of Artifacts," Final Report to the Getty Conservation Institute.

6. Baker, Mary T., "Potential of Adverse Effects of Pest Control Agents on the Materials of Artifacts," Final Report to the Getty Conservation Institute, March, 1989.
7. Derrick, Michele, "Potential of Adverse Effects of Pest Control Agents on the Materials of Artifacts," Getty Conservation Institute Final Report, October, 1989.
8. Cady, G. H. and S. Misra, "Hydrolysis of Sulfuryl Fluoride," Inorganic Chemistry, vol. 13, no. 4, (1975) pp. 837-841.
9. Padma, D. K., V. S. Bhat and A. R. V. Murthy, "Reactions of Sulphuryl Fluoride, Sulphuryl Chlorofluoride and Sulphuryl Chloride with Amines", Journal of Fluorine Chemistry, vol. 20, no. 4, (1982) pp. 425-437.
10. Meikle, R. W., "The Fate of Sulfuryl Fluoride in Wheat Flour", Journal of Agricultural and Food Chemistry, vol. 12, no. 5, (1964) pp. 464-467.
11. "Vikane Fumigation Manual", The Dow Chemical Company, 1982.
12. Scheffrahn, R., Osbrink, W., Hsu, R. and Nan-Yao Su, "Desorption of Residual Sulfuryl Fluoride from Structural and Household Commodities by Headspace Analysis Using Gas Chromatography", Bulletin of Environmental Contamination Toxicology, vol. 39 (1987) pp. 769-775.
13. Burgess, H. D. and N. E. Binnie, "The Development of a Research Approach to the Scientific Study of Cellulosic and Ligneous Materials", accepted for publication in the Journal of the American Institute for Conservation, vol. 29, no. 2, 1990.

ABSTRACT

The use of AGELESS®, a commercial oxygen absorber, as a means of generating low oxygen atmospheres for the treatment of insect infested museum objects is discussed. Previous studies have shown that prolonged exposure to low oxygen atmospheres is lethal to a wide range of insect species and their various developmental stages. Mixed cultures containing approximately equal numbers of different development stages of a number of common museum pests were sealed in a high barrier, plastic laminate with AGELESS® for three weeks at 30C. The oxygen concentration was reduced to less than 0.05% while one hundred percent mortality was observed for all insect species. AGELESS® proved to be a safe and effective means of generating low oxygen atmospheres though its application is limited in the case of large museum objects which when packaged possess a high internal air volume.

KEYWORDS

fumigation, pest control, controlled atmosphere, inert atmospheres, museum pests

INERT ATMOSPHERE DISINFESTATION USING AGELESS® OXYGEN SCAVENGER

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INTRODUCTION

Until relatively recently, ethylene oxide has been one of the most widely employed chamber fumigants for the control of insect infestations in museum collections. Because of its hazardous properties, and increasing evidence that exposure to ethylene oxide will damage museum objects, its use has been restricted and in many cases discontinued by a number of museums and cultural institutions (1-4). Given the above, various alternatives have been suggested including the use of low oxygen atmospheres. Low oxygen atmospheres have been used as an alternative to chemical fumigants for controlling insect infestations in grain and various packaged commodities with some success for a number of years. Studies on stored product pests have shown that prolonged exposure to low oxygen atmospheres (<0.5%) is effective against a wide variety of insect species and their developmental stages (5-7). A tentative treatment schedule based on the most tolerant species, *Sitophilus granarius* (Linnaeus), has been proposed, requiring an exposure time of at least 20 days to an oxygen deficient atmosphere (0.1% oxygen) at temperatures ranging from 20-29C (8).

Recent studies on various museum pests have yielded similar results. Insect cultures containing approximately equal numbers of different developmental stages of *Anthrenus vorax* (Linnaeus), *Stegobium paniceum* (Linnaeus), *Lasioderma serricornis* (Fabricius), and *Tineola bisselliella* (Hummel) were purged with nitrogen gas (<0.5% oxygen) at 30C for 1, 2 and 3 weeks (9). One hundred percent mortality was observed in all cases. More recent quantitative studies in which all developmental stages of four of the above species [*Anthrenus vorax* (larvae and eggs only), *stecobium paniceum*, *Lasioderma serricornis* and *Tineola bisselliella*] were tested, yielded similar results following purging with nitrogen gas (<0.5% oxygen) for 3 weeks at 30C (10).

From a practical standpoint the use of a low oxygen atmosphere to treat insect infested museum objects presents a number of difficulties. Purging a chamber with nitrogen gas requires an airtight seal to maintain the nitrogen concentration above 99.5% which may prove difficult to achieve. Burners or catalytic generators have also been used in the stored product industry to generate oxygen-free atmospheres with some success (11). Their adoption, however, would involve a large initial investment which may prove prohibitively expensive. One alternative is the use of oxygen scavengers. The latter have recently found widespread application in the food industry as an alternative to traditional nitrogen purging and vacuum packaging techniques for preserving dry foods. One of the most widely employed oxygen scavengers is manufactured and distributed under the registered trade name of AGELESS® by the Mitsubishi Gas Chemical Company of Japan.

In the following study, the use of AGELESS® as a practical means of generating low oxygen atmospheres for the treatment of insect infested museum objects was investigated. To this end a series of qualitative tests were conducted whereby mixed cultures containing approximately equal numbers of different development stages of various museum pests were exposed to low oxygen atmospheres inside high-oxygen-barrier plastic bags for three weeks at 30C using AGELESS®. The advantages and disadvantages of using oxygen scavengers for disinfesting museum objects are discussed in terms of these experimental trials.

AGELESS® AND AGELESS®-EYE

AGELESS® is described by Mitsubishi as a chemical oxygen scavenger prepared from powdered iron oxide which rapidly absorbs atmospheric oxygen (12). According to Mitsubishi, AGELESS® is capable of reducing the oxygen concentration in a closed bag or container to less than 0.01% and will maintain this level indefinitely depending upon the permeability of the packaging material. It is recommended as an alternative to nitrogen gas packing for a wide range of food stuffs and is described as a safe means of inhibiting aerobic micro-organism growth, the oxidation of fats and oils and as a means of killing insects.

Different types of AGELESS® are available depending upon the water activity (AW)¹ of the packaged commodity. AGELESS Z® is recommended for the preservation of dry food products possessing a water activity of 0.85% or less while AGELESS S® is recommended for food products possessing a water activity of 0.65% or more. AGELESS FX® is recommended for moist foods possessing a water activity of 0.85% or more.

AGELESS® is also available in different sizes depending upon the amount of oxygen to be scavenged. The amount of oxygen that can be absorbed is indicated (in milliliters) by the AGELESS® type number. Thus, AGELESS Z-200® is capable of absorbing the 200ml of oxygen contained in one liter of air. If there is some leakage, a smaller volume can be scavenged free of oxygen until the excess AGELESS® is used up.

For use in conjunction with AGELESS®, the Mitsubishi Gas Chemical Company also markets a product referred to as AGELESS-EYE®. It is described as an oxygen indicator and is used as a simple, qualitative test for determining the presence or absence of oxygen. It is manufactured in tablet form and slowly changes colour in the absence or presence of oxygen. The indicator gradually turns pink as the oxygen concentration is reduced to less than 0.1% but turns blue almost immediately as the oxygen concentration increases above 0.5%.

METHODS AND MATERIALS

INSECT CULTURES

Stock cultures of *Anthrenus vorax*, *Stegobium paniceum*, and *Lasioderma serricorne* were obtained from the Stored Grain Research Laboratory, CSIRO Division of Entomology, Canberra, ACT.

Stock cultures of *Tineola bisselliella* were obtained from the Department of Entomology, University of New South Wales, Sydney, New South Wales.

Anthrenus vorax was reared at 25°C and 70% RH on a culture medium consisting of 5g brewers' yeast, 1g Wesson salt, 1g cholesterol and 93g casein. A 2cm layer of cracked wheat was sprinkled over the top and a Savoiardi® Sponge finger biscuit was placed on the surface of the medium. *Lasioderma serricorne* and *Stegobium paniceum* were reared at 25°C and 70% RH on a culture medium consisting of 90g cracked wheat and 10g brewers' yeast. *Tineola bisselliella* was reared at 25°C and 62% RH on a culture medium, consisting of 180g casein, 20g brewers' yeast, 2g cholesterol and 10g chopped wool prepared from scoured, undyed top.

For experimental purposes, mixed cultures consisting of approximately equal numbers (50) of different developmental stages of *Anthrenus vorax*, *Stegobium paniceum*, *Lasioderma serricorne*, and *Tineola bisselliella* were prepared. To obtain sufficient numbers of larvae, pupae and adults a sequence of test material was first established by placing one hundred adult insects on approximately 200g of culture medium and then removing the adults one week later. New cultures were then set up each alternate week. From these cultures, larvae, pupae and adult insects were collected by hand.

Eggs of *Stegobium paniceum*, *Lasioderma serricorne*, and *Anthrenus vorax* were obtained by placing young adults on approximately 10g of finely sieved (60 mesh) cracked wheat. After 24 hours the eggs were collected by sieving. Eggs of *Tineola bisselliella* were collected by inverting a jar containing 100 adult moths over a 20 mesh screen. The eggs were laid through the screen and collected in a petri dish below.

EXPOSURE PROCEDURE

The mixed cultures were transferred to plastic bags (30cm x 15cm x 2cm) containing approximately 200g of culture medium. The bags were prepared from sheets of polyvinylidene chloride coated, biaxially oriented nylon (oxygen permeability = 3-5cc/m²/24hours at 20-25°C) whose edges had been heat sealed along all four sides. Prior to heat sealing the top edge, a packet of AGELESS Z-

¹ AW = R.H./100% where R.H. is the equilibrium relative humidity of the enclosed airspace within the packaged commodity and AW is expressed as a decimal fraction.

200*² and AGELESS-EYE® were enclosed along with a relative humidity indicator card. The control cultures were similarly prepared but without the addition of AGELESS®.

All cultures were then placed inside glass jars to prevent the escape of any insects which may have broken through the bags. The jars were then placed in a convection oven at 30C for three weeks. During this time the relative humidity inside each bag was monitored.

The oxygen content of the plastic bags containing the mixed cultures was determined at weekly intervals using a Food Bag Sampling Gun (Teledyne Model 340/RC Portable Oxygen Analyzer). After three weeks the glass jars containing the mixed cultures were removed from the oven and the plastic bags were cut open. The glass jars were then fitted with filter paper lids and incubated under controlled environmental conditions for an indefinite period.

RESULTS AND DISCUSSION

The results of the experimental trials with the various mixed cultures are given in Table I. The oxygen content of the mixed cultures in the sealed plastic bags in the presence of AGELESS® was reduced from approximately 21% to less than 1% (This proved to be the detection limit of the portable oxygen analyzer. Subsequent analysis by gas chromatography yielded an oxygen concentration of less than 0.05%). Furthermore, this level was maintained throughout the entire three week exposure period. These results are consistent with previously published findings for AGELESS® Z-200 in which the oxygen concentration in sealed plastic bags of similar size to the above was reduced from approximately 21% to less than 0.05% after 24 hours at 0%, 50% and 70% RH (13).

Over the same period of time, the oxygen content within the control cultures gradually decreased. This may be attributed to the high insect density within the sealed bags and the subsequent loss of oxygen through respiration (14,15).

Table I Lethal effect of AGELESS® on four common museum pests

Species	AGE-LESS® present	Oxygen conc. (%)			R.H (%)	Mortal-ity %
		1 wk	2 wk	3 wk		
<i>A. vorax</i>	+	-0-	-0-	-0-	60	100
<i>A. vorax</i>	-	10.5	2.5	1.1	60	-
<i>S. paniceum</i>	+	-0-	-0-	-0-	60	100
<i>S. paniceum</i>	-	14.5	6.5	2.6	60	-
<i>L. serricorne</i>	+	-0-	-0-	-0-	60	100
<i>L. serricorne</i>	-	12.5	5.0	3.2	60	-
<i>T. bisselliella</i>	+	-0-	-0-	-0-	50	100
<i>T. bisselliella</i>	-	10.5	7.5	4.0	50	-

The insect activity within the mixed cultures containing AGELESS® at first increased and then ceased several hours later as paralysis occurred in response to the reduced oxygen concentration within the sealed bags. No fresh emergences were observed in any of these cultures even after incubation under controlled

² The oxygen content of the sealed plastic bags was estimated using the following formula (12):

$$\begin{aligned}
 \text{Oxygen (ml)} &= [(\text{length} \times \text{width} \times \text{height}) - (\text{weight of product/spec. grav.})] \times 1/5 \\
 &= [(30\text{cm} \times 15\text{cm} \times 2\text{cm}) - (200\text{g} / 1\text{g/cm}^3)] \times 1/5 \\
 &= 120 \text{ ml}
 \end{aligned}$$

environmental conditions for several months following exposure to low oxygen atmospheres. The control cultures, on the other hand, remained active until the third week when the oxygen concentration fell to less than 4%. Subsequent incubation of the control cultures resulted in fresh emergences though initially they were few in number.

The relative humidity within the plastic bags containing the various mixed cultures decreased by approximately 10% due to the increase in temperature during the exposure period but otherwise remained relatively constant both in the presence and absence of AGELESS® due to the buffering action of the culture medium.

CONCLUSION

Given the above, it is readily apparent that AGELESS® can be used as a practical means for generating low oxygen atmospheres for the treatment of insect infested museum objects. The use of AGELESS® to generate low oxygen atmospheres possesses a number of advantages over nitrogen purging or the use of inert atmosphere generators. In particular, it is a safe and effective means of generating low oxygen atmospheres and requires relatively little technical expertise in its application. Moreover, it does not require the use of an airtight chamber. Because AGELESS® acts as a scavenger, it is also residue free.

Though all objects undergoing disinfestation with AGELESS® must be individually packaged in airtight bags, this is a relatively simple task and can easily be accomplished using a conventional heat sealer. A wide variety of high oxygen barrier plastic films are commercially available and can be readily obtained in sheet or roll form or even preformed bags. In general barrier films possessing an oxygen permeability of 20cc/m²/24hours or less are recommended if a low oxygen atmosphere is to be maintained for longer than two weeks (12). Depending upon the plastic film, keeping the object in the plastic bag will also prevent any reinfestation from occurring during storage. This would also prevent the subsequent spread of an infestation in the event of the failure of AGELESS® to achieve one hundred percent mortality.

The use of AGELESS® as a means of generating low oxygen atmospheres for treating insect infested museum objects does however have its limitations particularly with regard to the treatment of relatively large three dimensional objects. While it is possible to construct large airtight plastic bags from single sheets of plastic film using a conventional heat sealer, if the internal air volume is high (>10 liters) a prohibitively large number of AGELESS® packets may be required to achieve a sufficiently low oxygen concentration. Under these circumstances it may be possible to first reduce the air volume by purging with nitrogen or by partially evacuating the bag. Preliminary trials employing this approach have yielded promising results and are being pursued further.

MATERIALS AND SUPPLIERS

AGELESS®. Available from Swifts, Watts, Winter Company, 85 Egerton Street, Silverwater, New South Wales, 2141, Australia.

Teledyne Model 34OB/RC Portable Oxygen Analyzer. Teledyne Analytical Instruments, 16830 Chestnut Street, City of Industry, California, 91748, USA.

Cholesterol. Available from BDH Chemicals Ltd, 242 Beecroft Road, Epping, NSW, Australia.

Brewers' Yeast. Available from H. Langdon and Co., 77 Chapel Street, Lakemba, NSW, Australia.

Casein. Available from Milk Powder Distributors, 34 Burton Street, Mison Point, NSW, Australia.

Wesson Salt Mixture W. Available from Mallinckrodt Australia Pty Ltd, 27 Branks Street, Meadowbank, NSW, Australia.

Savoirdi® Sponge Finger Biscuit. Manufactured by Aurora Biscuits Pty Ltd, 44 Shepherd Street, Merrickville, NSW, Australia.

REFERENCES

1. M.L. Florian, "The effect on artificial materials of the fumigant ethylene oxide and freezing used in insect control", in Eighth Triennial Meeting of the International Council of Museums Committee for Conservation, Sydney, Australia, 6-11 September, 1987, ed. K. Grimstad (Los Angeles: The Getty Conservation Institute, 1987) 199-208.
2. A.W. Postlethwaite, "Fumigation, choice of fumigant and design of facility", in Eighth Triennial Meeting of the International Council of Museums Committee for Conservation, Sydney, Australia, 6-11 September, 1987, ed. K. Grimstad (Los Angeles: The Getty Conservation Institute, 1987) 1189-1196.
3. M.W. Ballard and N.S. Baer, "Ethylene oxide fumigation: results and risk assessment", Restaurator, 7, (1986)143-168.
4. "OSHA sets peak for ethylene oxide", Art Hazard News 2 (1988)1 3.
5. S.W. Bailey and H.J. Banks, "The use of controlled atmospheres for the storage of grain", in Proceedings of the 1st International Working Conference on Stored Product Entomology, (Savannah: Permanent Committee of the International Conference on Stored Product Protection, 1974) 362 -374 .
6. S.W. Bailey and H.J. Banks, "A review of recent studies of the effects of controlled atmospheres on stored product pests", in Controlled Atmosphere Storage of Grains, ed. J. Shejbal (Amsterdam: Elsevier, 1980) 101-118.
7. H.J. Banks, "Modified atmosphere and hermetic storage-effects on insect pests and the commodity", in Proceedings of the Australian Development Assistance Course on the Preservation of Stored Cereals, ed. B.R. Champ and E. Highley (Canberra: CSIRO Division of Entomology, 1984) 521-532.
8. P.C. Annis, "Towards a rational controlled atmosphere dosage schedules: a review of current knowledge", in Proceedings of the 4th Working Conference on Stored Product Protection, Tel Aviv, Israel, September 21-26, 1986, ed. E. Donahaye and S. Navarro (Tel Aviv: Permanent Committee of the International Conferences on Stored Product Protection, 1986) 128-148.
9. M. Gilberg, "Inert atmosphere fumigation of museum objects", Studies in Conservation, 34, no. 2 (1989)1 80-84.
10. M. Gilberg, unpublished results.
11. H.J. Banks, "Current methods and potential systems for production of controlled atmospheres for grain storage", in Controlled Atmosphere and Fumigation in Grain Storages, ed. B.E. Ripp et al. (Amsterdam: Elsevier, 1984)' 523-542.
12. AGELESS® OXYGEN ABSORBER: A New Age in Food Preservation [brochure] (Tokyo: Mitsubishi Gas Chemical Company, 1987).
13. M. Gilberg, "AGELESS® oxygen scavenger", AICCM Newsletter, 32 (1989)1 6.
14. H.J. Banks, "Hermetic storage", in Proceedings of the Australian Development Assistance Course on the Preservation of Stored Cereals, volume 2, ed. B.R. Champ and E. Highley (Canberra: CSIRO Division of Entomology, 1984) 558-573.
15. T.A. Oxley and G. Wickenden, "The effect of restricted air supply on some insects which infest grain", Annals of Applied Biology, 51 (1963) 313-324.

ABSTRACT

A comparison of museum pests in the United States and in Southeast Asia is made. The relationship between the climate and the collection is reviewed. Their effect on museum pest control strategies is discussed, including the ramifications for treatment and for international loan exhibitions.

KEYWORDS

Pest Control, Tropical, Climate, Temperate, Environment.

PEST CONTROL FOR TEMPERATE vs. TROPICAL MUSEUMS: NORTH AMERICA vs. SOUTHEAST ASIA

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Introduction

Pests which damage art works and artifacts are a cause of concern to museums and archives throughout the world. The aggregation of large numbers of similar objects in a single collection space can attract and maintain a large pest population. Similarly, the conditions for the optimum preservation of the objects can be simultaneously the preferred climate for pest growth. Climate itself can affect the type and species of most prevalent pest, and thus, which museum objects are most at risk. In order to develop a pest control strategy, the types of pests that threaten a collection need to be identified and reviewed.

Climate and Collection Specific Pests

Table I summarizes the major differences between North American and Southeast Asia museum pest problems. A great deal of North American and European literature on pest control in museums involves the control of textile pests (9). These textile pests are divided into two families: the dermestids called carpet beetles (*Anthrenus* and *Attagenus*) and the clothes moths (*Tineola bisselliella* H. and *Tinea pellionella* L.) (See Figures 1 and 2). These insects attack keratin, the sulfur containing amino acids found in wool, hair, and camelid fibers (sheep wool, llama, alpaca, vicuna, camel, and goat hair products).

Because of the climatic conditions of the Americas and Europe, both wool and camelid fibers are seasonally used today in clothing and furnishings and were used in the past. Thus, not only do museum staff and visitors wear wool clothing subject to infestation, but also large portions of American and European textile collections have such fibers--tapestries, carpets, folk art and archeological objects, military uniforms and flags--as their principal component, or as part of the object--as the batting inside quilts and as stuffing in upholstered furniture.

These collections are constantly threatened by the infestation of keratin-eating insects, particularly those objects with soiled fabrics or those with brushed (napped) surfaces. Staff and visitors can inadvertently introduce such pests to the museum environment and also provide the keratin-based fiber dust to support the initial growth.

Consequently, it is extremely important for museums in temperate climates to maintain a dust-free environment. This concept is so engrained that the museum staff and the general public alike associate dust with insects and vermin. Textile objects are routinely examined and vacuumed to reduce the hazard of insect infestation. Isolating textiles by means of storage containers (i.e. wrapped in acid free tissue paper and then boxed) is oftentimes the preferred textile storage method.

In Southeast Asia, keratin-containing fibers are not an indigenous fiber source for fabrics. Both modern usage and antique collections are restricted largely to cellulosic materials (cotton, abaca, ramie, hemp) or silk. The latter does not contain a significant cysteine or methionine amino acid content. Thus, dust in the Southeast Asian domestic environment and in the museum environment does not foster the same pest control problem.

By contrast, silverfish, a minor pest for most American libraries, archives, or museums, can constitute a more sizable problem in ASEAN* countries where they can threaten paper, books, textiles, and basketry. Open aggregations of materials like library stacks or archival collections are particularly at risk. Tropical conditions do not provide a cold season "kill" of the insects in their outdoor harborages. This is also true of cockroach harborages. While American museums can often restrict pest control operations to specific basement or food handling areas, ASEAN

*Association of Southeast Asian Nations: Singapore, Indonesia, Malaysia, Thailand, The Philippines, and Brunei.

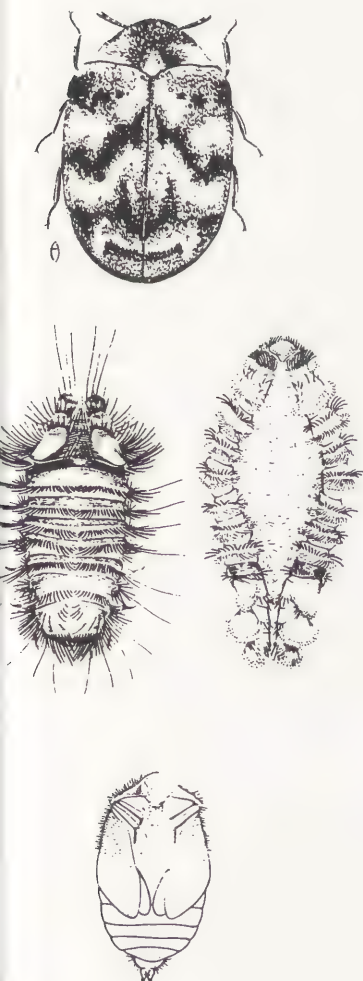


Figure 1. Varied Carpet Beetle, *Anthrenus verbasci*, L.: Adult (2-mm long), larva, pupal skin, and pupa. After Story (9).

museums have formulated several policies and procedures to reduce this threat of infestation. Restrictions on the use of photocopies, extraneous paper files, and memoranda are routine.

In ASEAN countries these precautions are natural to everyone there: coffee and tea cups are lidded when not in use; waste-paper baskets are emptied twice daily; desks are wiped down, as are floors. Gallery openings are catered with food located outside the museum building. In Singapore, the common species are the American cockroach (*Periplaneta Americana*), the German cockroach (*Blatella Germanica*), and the Oriental cockroach (*Blatta Orientalis*) (1, 2, 5).

Although wood-boring beetles (*Anobium punctatum* DeG. and *Lyctus* spp.) are major pest problems in European museums and historic buildings, they have not been a serious problem for collections in the United States. With the ban of chlorinated insecticides, however, this type of insect infestation is an increasing concern. Painting stretchers as well as furniture have been infested; American furniture conservators are trained to identify the characteristic frass and bore-holes of these pests. ASEAN conservators are rarely faced with those wood boring beetles because of the extensive use of the insect resistant woods traditionally employed by artists and craftsmen. This extensive use of tropical hardwoods, like teak, both in the museum furnishings such as cabinets and display cases and in the antiques themselves, including the Chinese furniture, has meant that the ASEAN collections are largely free of this hazard.

Termites, however, can attack structural components of the tropical museum buildings and Western-type wood display cases. Anecdotal evidence of rapid damage continues to be exchanged among S.E. Asian conservators. This damage may be caused by subterranean or drywood termites (e.g. *Coptotermes curvignathus* H. and *Cryptotermes cynocephalus* L.). Historic structures in North America are most likely to be damaged by the Eastern subterranean termite (*Reticulotermes flavipes*, Kollar) where the average minimum winter temperatures do not reach -29°C. (4, 10).

Another major hazard to ASEAN museum collections is a small (2mm) insect, the "cigarette beetle" (*Lasioderma serricornes* F.), which routinely attacks tropical collections of bamboo and rattan (Figure 3). The breadth of the infestation threat that these insects pose is most readily apparent when Western observers remember that, historically, South East Asia was prized for its spice growing: these *Anobiidae* not only feed on spices but are also characterized as the most destructive members of the *Anobiidae* family (7). Pest control for cigarette beetles, therefore, includes chemical treatment. Insecticides, with their residual protection, are preferred by conservators over fumigation for basketry (3).

Implications for Treatment and International Loans

Objects and packing materials transported from one museum to another within a single climatic region bring certain entomological risks. With similar collections and similar climates, the prevalent and most serious infestation problems will be similar. At both the origin and the destination, conservators and registrars will examine the crates for the same insect problems. Otherwise, untreated infestations could spread to the host museum's collections.

When objects and packing materials travel abroad, particularly across climatic boundaries, the entomological implications may be more difficult to recognize. The conservators and registrars may be unfamiliar with the signs of infestation; they will certainly be less familiar with treatment. While the host museum's collections may be at a lower risk due to its dissimilar materials and external climate, the incoming loan may be less well monitored. For example, the protocols for woolen textiles would not be familiar to staff at the National Museum, Singapore nor would the characteristics of incipient infestation. Any carpet beetle or moth infestation that arrived with a loan shipment might not be an issue for the Singaporean collections, but could cause serious damage to the loaned textiles. Similarly, textiles being returned to an ASEAN museum from the West might be carefully rolled on acid free tubes, wrapped in acid free paper, and packed in acid free cardboard containers. Such a shipment is standard and acceptable in temperate regions, but would be an ideal harborage for local pests in South East Asia.

Perhaps more important, such loans may be subject to minor repairs with inappropriate materials. Thus, a tropical museum's basketry loaned to a temperate

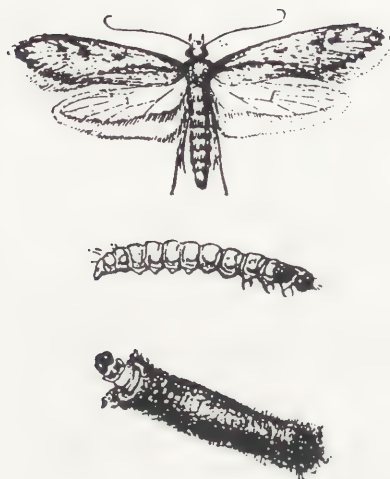


Figure 2. Adult, larvae, and case of casemaking clothes moth, *Tinea pellionella*, L. Wing expanse is 10-14mm. After Story (9).

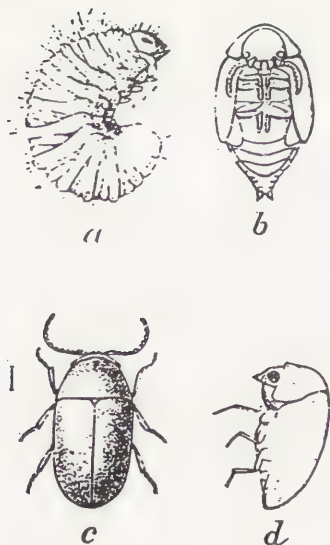


Figure 3. Cigarette beetle, *Lasioderma serricornes*, F. (a) is the larva; (b) the pupa; (c) and (d), the adult (2-3mm long). After Story (9).

climate museum might be repaired without consideration of the need for close monitoring in its ASEAN home; textiles might be permanently mounted with corrugated acid free board, a procedure acceptable in North America where the cockroach and silverfish problems are not severe. Temperate climate conservators cannot predict the possible synergism between their "safe" conservation materials and unknown pest populations.

Conclusion

The conservation field must be prepared to recognize not only the insect hazards to collections in their home institutions, but also the implications of these hazards to other institutions abroad. Particularly important with the present tendency for loans and exhibitions across climates, is the need for a recognition of inherent differences. Museum construction, policies, monitoring, laboratory activities, gallery design, storage, and exhibitions, and even preventive measures may well have been created to deal with specific indigenous insect problems. Conservation treatment programs developed locally must be evaluated in light of their response to specific biodeterioration threats characteristic of the climate within which the local museum, its collections, and its conservators live and work. Registrars and conservators are oftentimes surprised at the choice of packing materials from cross-climate institutions. Rarely are they aware that the selection may be due to a knowledge of local insect proclivities, rather than a lack of more "appropriate" supplies.

Museums in both climatic conditions need to be more observant and more forthright about the potential insect hazards in their climatic zone. It is not enough to request permission to fumigate nor is it useful to recommend a particular type of pesticide, unless the insect pest is actually identified and the dosage necessary to eradicate that particular species is clearly determined. Long term effects of even relatively benign agents can be serious (6,8). The actual chemical treatment technology can only be properly transferred under carefully prescribed conditions. The conservation treatment preparatory to an exhibition cannot be effectively transferred without careful assessment of the potential biodeterioration mechanisms of the climatic zones involved. The museum environment exists within a larger climatic and biological zone; that larger zone may be forgotten only at the risk of irreparable damage to cultural patrimony.

Pest Control References

1. Chew, Tee Sim. National Museum, Singapore. Communications December, 1988 and January, 1989.
2. Chong, Patrick. Rentokil Pte Ltd., Singapore. Communications, December, 1988, and September, 1989.
3. Core Manual, Maryland Pesticide Applicator Training Series. College Park, Maryland: University of Maryland, 1986/7.
4. Dynamac Corporation. Structural Pest I: Termites. National Park Service Information Package. September, 1984.
5. Lee, R. Managing Director, SGS AllPest Management Pte Ltd., Singapore. Communications, December, 1988.
6. "Naphthalene," Chemical Fact Sheet. Cambridge, MA, USA: University Health Services, Environmental Health and Safety, Harvard University, 1983.
7. Meltzer, J. Technical Services, Smithsonian Institution. Ccommunication, April, 1989
8. "P-Dichlorobenzene," Chemical Fact Sheet. Cambridge, MA, USA: University Health Services, Environmental Health and Safety, Harvard University, 1983.
9. Story, K.O. Approaches to Pest Management in Museums. Washington, D.C.: Smithsonian Institution, Conservation Analytical Laboratory, 1985.

10. Supriana, N. "Studies on the Natural Durability of Tropical Timbers to Termite Attack," International Biodeterioration, vol 24 (1988): 337-341.
11. van de Hoop, A.N.J. "Raffles Museum, Singapore: Report on a Mission to the Raffles Museum, Singapore from October 23, 1956 to January 14, 1957. Paris: Technical Assistance Department, UNESCO (unpublished report).
12. Wiencke, V. and A. Martini, Desowag Materialschutz GmbH, Düsseldorf, Bundesrepublik Deutschland. Communication, December, 1988.

TABLE I.
Types of Pests
Common Museum Pest Control Problems

<u>Object</u>	<u>Insect</u>	<u>North America</u>	<u>ASEAN Region</u>
Basketry	Cigarette beetle	rare	critical
Paper	Silverfish	rare	critical
	Cockroach:		
	American	occasional	common
	Asian (southern USA)	occasional	N.A.
	Brown-banded	occasional	N.A.
	Brown	occasional	N.A.
	German	occasional	common
	Oriental	occasional	common
Structures	Termites:		
	Subterranean	occasional	critical
	Drywood	rare	critical
Textiles (wool, hair)	Carpet beetles	critical	rare
	Clothes moths	critical	rare
Wood:			
Softwood	Furniture beetle	occasional	N.A.
Hardwood	Furniture beetle	occasional	N.A.
	Powder-post beetle	occasional	N.A.*

Notes:

N.A. means Not applicable, i.e. not indigenous.

*Not listed as indigenous to ASEAN countries, but capable of attacking bamboo.

References: 1, 2, 4, 9, 10.

ABSTRACT

An alternative method of fumigation using an inert atmosphere, nitrogen, has been investigated for eliminating insect infestations in museums and archival collections. The lethal effect of nitrogen as anoxant for insects has been determined under controlled temperature and relative humidity conditions using three systems: plastic bags of low permeability, a traditional fumigation vacuum chamber and an experimental metallic chamber.

In all cases analyzed, nitrogen was found an effective method for eradicating common fauna, such as the furniture beetle, *Anobium punctatum* from cellulosic materials. The efficacy of the system is being analyzed in a pilot project which includes the treatment of a large collection of archival materials infested by members of the beetle order, Coleoptera. This inexpensive method is safe and reduces chemical alteration in the treated objects.

INSECT ERADICATION IN MUSEUMS AND ARCHIVES BY OXYGEN REPLACEMENT, A PILOT PROJECT

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INTRODUCTION

Fumigation by insecticides and pesticides is the most common method of insect control. However, very often these agents present serious disadvantages involving operator safety during the fumigation treatment and the safety of person handling fumigated objects (1). Chemicals used in environmental disinfection of museum collections have only limited efficacy because of their low penetration in books, sculptures, or paintings (2). Moreover the literature shows deleterious effects of the common insecticides on the treated materials (3,4).

Recent investigations have demonstrated that the displacement in air of the oxygen by nitrogen produced a lethal effect in all the stages of the life cycle of the fruit fly, *Drosophila melanogaster*, an insect used as a model, exposed to controlled relative humidity (RH), temperature, and oxygen level (40% RH, 30°C, and 0.5% oxygen concentration) for 30 hours incubation (5). It was also reported that a nitrogen atmosphere was effective for eliminating the termite, *Cryptotermes brevis*, found in contaminated pieces of wood when exposed to 40% RH, 25°C, 1% oxygen concentration and incubated for 3 weeks (6).

In an extension of this work, comparative analyses have been carried out using nitrogen at controlled conditions for eradicating insect populations in a large collection of archive materials mainly contaminated by *Anobium punctatum*. Our aim has been to determine the efficacy of nitrogen as anoxant for eliminating insects, and the optimum method for using inert gases in archives and museums.

MATERIALS AND METHODS

Materials

Cellulosic materials such as books, and bundles of papers infected with eggs, larvae, pupae and adults from *Coleoptera*, *Anobium punctatum* which were exposed to a nitrogen atmosphere have been analyzed.

Methods

Groups of books of identical size (28 cm x 35 cm x 7 cm) were infested with *Anobium punctatum* cultured under laboratory conditions. The same number of insects in each stage (adults, larvae, pupae and eggs in the last maturation phase) were developed in the books (4 cm deep) as a substrate. Quantification of mortality was made stage-specific at the different conditions.

Plastic bag of low permeability

Based on the method described by Valentin and Preusser (7), the contaminated material was placed in a sealed bag made of polyethylene terephthalate of low permeability and purged with nitrogen at 250 ml/min to replace air by the inert gas at 35% RH 30°C for 8 hours. The plastic bags were hermetically sealed and incubated at room conditions for 5, 10, and 15 days. Oxygen absorber (Ageless®, Mitsubishi International) was used to maintain the oxygen concentration at very low levels. After exposure to nitrogen, the material was exposed to ambient air for ten weeks to evaluate the mortality of the insects. The average oxygen level during the treatment was 0.9%. A second group of contaminated books was purged with air at identical conditions and used as a control.

Experimental metallic chamber

In parallel experiments, a metallic chamber (750 x 500 x 500 cm.) was designed to study the efficacy of nitrogen on infested material collections, and determine how long the insects' exposure to low oxygen concentration should be. A chamber made of stainless steel with a glass window equipped with RH, temperature and oxygen sensors was used to reproduce the specific archive conditions. In this case our goal was to determine the optimum conditions for a particular infestation. In

particular, the optimum incubation time in relation to the specific insect and type of material can be easily determined.

Fumigation vacuum chamber

A vacuum chamber, 3105 liters, with computerized control for temperature, RH, vacuum and pressure was also used. Using the microprocessor system, all the parameters can be programmed, providing a wide range of precise conditions for optimizing and reducing the incubation time for all types of contaminated materials. The traditional fumigation vacuum chamber can thus be used in a manner in which nitrogen replaces the ethylene oxide, methyl bromide or sulfuryl fluoride fumigant normally used, offering conservators an alternative method which avoids the risk of toxicity and introduces the quicker nitrogen treatments.

RESULTS AND DISCUSSION

Using plastic bags of low permeability at the above conditions, 100% mortality was achieved in all the insects placed in books which were treated in a chamber purged with a nitrogen atmosphere and incubated for 10 days. This result agrees with previous data obtained using *Drosophila melanogaster*, and *Cryptotermes brevis* (8). It was shown that the combination of low RH and high temperature (30-35°C) under absence of oxygen had a drastic effect on the mortality of the treated insect. Identical results have been found for books contaminated by *Anobium punctatum* and treated in the metallic chamber. However, preliminary experiments show that the operation time necessary to achieve 100% mortality is reduced around 40% using fumigation vacuum chamber at 30°C temperature, 35% RH, pumped down to 1.5 g/cm² vacuum and refilled with nitrogen at 1 kg/cm² pressure.

It has been suggested that a combination of inert gases such as nitrogen with carbon dioxide, could improve the efficacy of nitrogen. The incubation time might be decreased because of the effect of carbon dioxide which increases the insects' respiration rate (9). This slight modification in our approach is being tested.

Insect control in archives. A pilot project

To validate our experimental results, a real case, the Archive of Reino de Galicia in Spain, with high infestation by *Coleoptera* has been used as model. The archive built in 1775, has six floors with 9000 m of selves. It was observed that approximately 20% of the total documentation was contaminated by *Anobium punctatum* and powder post beetles, *Lyctus spp.* in all the stages of the life cycle. During two years, disinfection treatment using insecticides in the environmental atmosphere reduced the number of adults and larvae per bundle of papers but this method was not effective for eradicating the infestation. Now, according to our experimental results nitrogen is being used in plastic bags under temperature and humidity control. A total of ten objects per day is being treated at the identical conditions explained above, and incubated for three weeks. Oxygen absorber, Ageless® (8,9), is also being used in each bag.

Preliminary results show that ten treatments using one contaminated bundle of papers per bag purged with a nitrogen atmosphere (250 ml/min), under 30% RH, 30 °C for 10 hours and 20 days incubation were effective in eliminating 100% of the insects in each treatment. The average number of live insects in each bundle was: adults 12.5, larvae 25.7 and pupae 10.6. Other treatments using an increasing number of contaminated archival materials per plastic bag and a shorter incubation time are in progress.

To complete this work other aspects are being studied such as:

- Ecology of the specific fauna in each stage of the life cycle.
- Statistical analysis to evaluate the efficacy of nitrogen for eliminating insects in the treated pieces.
- Relationship between nitrogen penetration and size of the treated pieces.
- New types of plastics and systems for treatment of a large number of archival materials.
- Environmental control and architectural solutions in the archive to reduce RH, and the risk of further reinfestation.

This treatment that is being used in the Archive of La Coruña for one year is an experiment in progress. Using the Archive of La Coruña model, other museums, archives and libraries will be included in this pilot program to study different

ecosystems and evaluate the efficacy of nitrogen for disinfecting large object collections.

CONCLUSION

A nitrogen atmosphere is an effective means for controlling insect infestation on cellulosic materials. 100% mortality of *Anobium punctatum* in all stages (stadia) of the life cycle was achieved on contaminated pieces exposed to 35% RH 30°C, and 1% oxygen concentration for 10 days incubation time. Using vacuum chamber the insects' exposure time to nitrogen necessary to achieve 100% mortality is significantly reduced.

Based on laboratory analyses a pilot project is being developed to eradicate insect infestation in archives, libraries and museums exposed to different environmental conditions and types of fauna.

This inexpensive method is an alternative to toxic gas fumigation, and can be used for systematic treatment of contaminated ancient objects.

ACKNOWLEDGEMENT

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REFERENCES

1. P. Peltz, and M. Rosol, "Safe Pest Control Procedures for Museum Collections". Center for Occupational Hazards. New York (1983) :1-8.
2. Z. Dvoriashina, "The Smirnov Beetle as a Pest in Libraries" Restaurator 9 (1988):63-81.
3. M. Florian, "The Effect on Artifact Materials of the Fumigant Ethylene Oxide and Freezing Used in Insect Control". Eighth Triennial Meeting of The International Council of Museums, Committee for Conservation, Sydney (1987):199-205.
4. A. Postlethwaite, "Fumigation Choice, of Fumigant and Design of Facility". Eighth Triennial Meeting of The International Council of Museums, Committee for Conservation, Sydney (1987):1189-1196.
5. N. Valentin and F. Preusser, "Insect Control by Inert Gases in Museum Archives and Libraries". Restaurator (1989). In press.
6. N. Valentin and F. Preusser, "Nitrogen for Biodeterioration Control on Museum Collections". (Paper delivered at the Third Meeting of the Pan American Biodeterioration Society, Washington August 3, 1989), 3. In press
7. Valentin, "Insect Control" 7.
8. Valentin " Nitrogen for Biodeterioration control". 29
9. M. Ali Niaze, "The Effect of Carbon Dioxide Gas Alone or in Combinations on the Mortality of *Tribolium Castaneum* (Herbst) and *T. confusum*. Journal of Stored Food, no. 7 (1971):243-52.
10. H. Nakamura, and J. Hoshino, "Techniques for the Preservation of Food by Employment of an Oxygen Absorber". In Sanitation Control for Food Sterilizing Techniques. Ed. Sanyu publishing Co., Tokyo (1983): 1-45.
11. Y. Oguchi, T. Sadahiro and J. Fukami, "Insecticidal Effect of the Oxygen Absorber Ageless® on Insects Injurious to Stored Grains". Institute of Physical and Chemical Research Tokyo. Report in preparation.

ABSTRACT

A series of compounds have been investigated in the entomological section of VNIIR for long term and efficient antifeedant activity, i.e. their tendency to prevent insects from feeding on otherwise desirable food materials. The antifeedant activity of a variety of compounds were tested on dermestid larvae, *Attagenus smirnovi* Zhant., and on clothes moth larvae, *Tineola bisselliella* Humm. under conditions of free food choice. Controls were made in the absence of antifeedants. The research found prospective antifeedants (tin-organic polymer latex "ABP-40*", polyguanidine "Metacide*", Carboxide and others) which could be used in museum practice. During the first year, the investigation revealed that the latex "ABP-40*" treatment was more effective for protection of small mammal skins than sodium arsenite.

KEYWORDS

Antifeedant, dermestid larvae, clothes moth larvae, tin-organic polymer latex "ABP-40*", sodium arsenite, polyguanidine "Metacide*", pyrocatechol compounds.

NEW ANTIFEEDANTS FOR PEST INSECTS IN COLLECTIONS AND VARIOUS ASPECTS OF THEIR USE IN MUSEUMS

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INTRODUCTION

The arsenal of chemical compounds used to protect museum objects from dermestid beetles (Coleoptera, Dermestidae) and clothes moths (Lepidoptera, Tineinae) is not very extensive. The number of pest populations resistant to insecticides has grown in the last years. Therefore, together with the development of a strategy of using available protective means, it is most urgent to develop the extension of the range of biologically active compounds, including antifeedants, with specific action.

The use of antifeedants is an efficient and selective method of protecting materials from the dermestid and clothes moth larvae. Antifeedants used in museums must have low-toxicity and a high antifeeding effect. At the same time they must not cause any changes in the physico-chemical properties of materials nor produce other undesirable side effects.

As a result of planned experiments, we determined that effective antifeedants for dermestid larvae and clothes moth larvae included the tin-organic polymer latex "ABP-40*", polyguanidine "Metacide*", Carboxide (a well-known repellent for blood-sucking insects) and some compounds isolated from natural sources.

An analysis of the literature and patents showed that low-molecular weight tin combinations (tetrabenzyl tin, tetraphenyl tin and others) can be used to protect woollen textiles from clothes moth larvae and dermestid larvae. However, they are more dangerous to warm-blooded animals than polymeric compounds. Polymeric tin-organic biocides of the general formula R_3Sn_x were produced in the Scientific Research Institute of Chemistry of Lobachevsky State University in Gorki. Their biocidal agent is represented by lateral functional groups R_3 which contain trialkyl or aryl tin. These are capable of forming oxides and hydroxides at a rate which is directly related to the water balance: it increases when the humidity of the material or the air rises. This mechanism depletes the original compound limiting its very long term effectiveness. Latex "ABP-40*" is a product of the copolymerization of tributyl tin acrylate with esters of acrylic and methacrylic acids. This preparation works well as a fungicide. An addition of 1-2% to manufactured polyvinylacetate and polyacrylate water-dispersed glues and paints protects them from microbiological deterioration. In addition, latex "ABP-40*" has a number of advantages which can be taken into consideration when introducing it into practice. The compound is only moderately toxic for warm-blooded animals, poses no danger of inhalation poisoning and has no effect on the physico-mechanical properties of materials.

The purpose of our investigation was to study the antifeedant effect of latex "ABP-40*" upon dermestid larvae on wool broadcloth, on felt and on the skins of small mammals. The study of the antifeedant effect of this compound was conducted according to the method described in detail in our earlier paper (1). Experiments were made on middle-stage dermestid larvae, *Attagenus smirnovi* Zant. taken from

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laboratory cultures. Latex "ABP-40*" was applied to samples of woollen broadcloth. Weight concentrations of copolymer (i.e., the relation of dry latex residue to the weight of a broadcloth sample) ranged from 0.0001% to 2%. Dermestid larvae were offered treated and untreated (control) pieces of broadcloth under the conditions of free choice and in the absence of choice. Experiments were made at controlled temperature and humidity.

The difference in weight of the sample before and after the experiment was an indicator of the feeding attractiveness of the broadcloth for the larvae. The antifeedant activity of the substances tested was determined by calculating the Ratio of Antifeedant Effect (RAE) by the formula:

$$\text{RAE \%} = 100(1 - E/C)$$

where E is the amount of treated woollen broadcloth eaten by the larvae in a given time and C is the amount for the untreated control.

RESULTS

In the first series of experiments on Latex "ABP-40*", we established the threshold of its effective concentration to be 0.1% to ensure reliable protection of a material against the larvae. In the absence of choice, RAE was $88.0\% \pm 5.0\%$. The experiments were repeated 22 months after the treatment. The results are summarized in table 1.

Table 1.

Latex "ABP-40*" Antifeedant effect on woollen broadcloth
22 months after the treatment

Time Months t	Weight Concentra- tion of ABP-40*	Weight of broadcloth eaten by larvae, mg		RAE %
		Experiment	Control	
0	0.1	n.a.	n.a.	88±5
0	0.5	n.a.	n.a.	99±1
22	2.0*	0.9±0.1	7.2±1.4	87±3
22	2.0	0.9±0.4	8.1±6.1	90±4
22	1.5	1.0±0.2	"	88±3
22	1.0	1.1±0.3	"	86±5
22	0.5	1.4±0.4	"	83±6
22	0.1	1.1±0.5	"	87±6

Note: * - this experiment was carried out in the absence of choice of food for the larvae.

Thus, it is evident that the organo-tin polymer, latex "ABP-40*", retains its antifeedant properties for 22 months and it can be included in the group of long-term antifeedants. At 22 months, the antifeedant characteristics of "ABP-40*" in the weight concentrations of 0.1%, 0.5% and 1% were somewhat lower than right after the treatment although they were still high. For comparison: $\text{RAE}_{0.5\%}(t=0) = 99 \pm 1\%$, and $\text{RAE}_{0.5\%}(t=22) = 83 \pm 6\%$. This fact shows the dynamics of organo-tin polymer latex decomposition, which is reflected by a change in their biological effect.

The results obtained show that reliable protection from dermestid larvae under laboratory conditions was ensured by small quantities of "ABP-40*" at a weight concentration of 0.1% and at a weight per unit area of 0.3 g/m^2 when uniformly applied to woollen broadcloth. This takes into account that most of the broadcloth samples were not damaged at all by larvae, and only few of the remainder were damaged slightly. As a mechanism, one can state that polymer latexes affect the larvae's contact chemoreceptors. The repulsion happens at the stage of them identifying the food substrate before a trial bite is taken.

For local treatment of auxiliary museum materials, a 1.5% - 2% weight concentration of latex "ABP-40*" needs to be used. Then there will be a guarantee of its residual effect for 22 months after the treatment.

The deterioration of natural science collections by keratophagous insects is the most common cause of the loss of their scientific and aesthetic value. Since the second half of the 18th century to the present, sodium arsenite has been the principal compound used to protect animal skins from deterioration by keratophagous insects. In the course of time, only the concentration of sodium arsenite solutions used in practice was changed: from saturated solutions in the past to 5-10% at present. This is, perhaps, one of the reasons why modern collection materials have, as a rule, insufficient resistance to pests. We investigated the antifeedant and insecticidal action of sodium arsenite and latex "ABP-40®" upon *Attagenus sminovi* larvae by the method described above. To make experimental samples, dried animal skins were soaked for 12 hours in the biocide solutions. Then they were then dried and offered to the insects as food. Data obtained from these experiments are summarized in Table 2.

Table 2.

Antifeedant effect of solutions of sodium arsenite and Latex "ABP-40®" in different concentrations upon skins of white mice and rats

Name of Solutions	Solution Concentration %	Amount of material eaten by larvae in experiment		Ratio of antifeedant effect (RAE) in % on skins	
		mouse skins	rat skins	mice	rats
Sodium Arsenite	2	1.8±1.2	3.6±2.0	73±14	0
	5	2.4±1.0	5.1±2.2	64±25	0
	10	2.7±0.8	6.1±3.7	60±26	0
APB-40®	0.5	0.12±0.04	0.8±0.7	98±2	78±21
	2	0.2±0.1	0.7±0.7	97±3	81±19
	5	0	0.8±0.8	100	0
Control	0	6.7±3.8	3.7±1.6	n/a	n/a

Note: Latex "ABP-40®" had a high antifeedant effect on both mouse and rat skins. The antifeedant effect of sodium arsenite on mouse skins was, as compared with that of latex, substantially lower, and the effect on rat skins was absent completely. Evidently the antifeedant effect of the two compounds appears to depend upon the species of animal whose skin has been treated.

In all of the experiments with ABP-40®, the mortality of dermestid larvae constituted 17-23% of the total number in the experiment. Maximum biocidal activity was observed in Petri dishes with skin samples treated with 2-5% latex solutions. The feeding of the larvae on mouse skins treated with 2%, 5% and 10% sodium arsenite solutions caused destruction of 10%, 57% and 63% respectively of the total number of the larvae involved in the experiment. When keeping the larvae on rat skins treated with sodium arsenite (2%, 5% and 10% solutions were also used), their mortality was 13%, 37% and 33% respectively. Thus, the larvae mortality when feeding on rat skins treated with 5% and 10% sodium arsenite solutions was half that in the experiments where the larvae were offered similarly treated mouse skins as food. So, latex has higher antifeedant but lower insecticide activity than that of sodium arsenate. Evidently, it is connected with differences in the mechanism of protection of these compounds. Latex, by affecting the contact chemoreception organs of insects, prevents the larvae from feeding. In some cases, however, trial biting-off of a material by the larvae still occurs. This accounts for a certain number of larvae dying in the experiment. Sodium arsenite, on the other hand, does not reduce the substrate food attractiveness. The toxic effect of this compound is revealed only by the larvae assimilating food. That is why the insects, before perishing, cause substantial damage to materials.

The purpose of the next series of experiments was to determine the protective effect of solutions of sodium arsenite and ABP-40® latex with different conditions of skin treatment. In the experiment, the least resistance to Dermestid larvae was shown by skins treated when they were freshly dressed. These rat skins acquired antifeedant properties only after a 12 hour soaking in a latex solution. The feeding experiments were repeated a year after the treatment. They showed that the antifeedant effect of latex upon skins was preserved at the 80-98% level a year later. On the contrary, the values of the RAE for skins, treated with a sodium arsenite solution rose up to 71-100%. Thus ABP-40® is, at least within the first

year after the treatment, a reliable method of protecting collection skins of small mammals. Its reliability is greater than that of sodium arsenite even with very low concentrations of solutions. Sodium arsenite has, within the first year after the treatment, less pronounced antifeedant characteristics as compared to latex. With the passing of time, however, its antifeedant effect rises. It is necessary to find out what is the reason for this effect and explore how steady this tendency is. Evidently, to protect skins of small mammals from biodeterioration it is advisable to use ABP-40*. To do so, it is sufficient to put the skins in a 5% latex solution for 5-10 minutes and then dry them with the help of starch and to comb them. Also it is possible to use 5-10% sodium arsenite solutions to protect skins of small mammals from pests. In so doing, however, one should bear in mind that long soaking of skins in a sodium arsenite solution can cause hair to fall out.

DISCUSSION

The antifeedant characteristics of the two compounds decrease when the skins of larger mammals are treated. This defect possibly can be eliminated by an increase in the time of treatment with the biocide. Also we think it is necessary to study the possibility of using ABP-40* latex to protect the skins of birds and reptiles, as well as natural materials utilized to make biogroups in museum. The latex use can be extended in scientific zoological collections for the treatment of dry osteological materials. It may limit food substrates for harmful insects in collections and thus prevent them from spreading through museum storage.

The organo-tin polymer Latex "ABP-40*" is of special interest as a compound having a biological effect upon a range of organisms harmful in museum conditions (insects, mold fungi, bacteria). It is of particular significance in regions with tropical climates and during the transportation of exhibits.

Polyguanidine "Metacide*", synthesized in the USSR, attracted our attention by the fact that it is soluble in water in any concentration, is non-toxic, used in medicine, and produced in the USSR from raw materials that are not in short supply. In addition, it is used in conservation and restoration practice for the biodeterioration protection from molds and fungi attack of paper and protein starch glues, as well as for black-and-white and colored film and photo documents stored in the archives.

Previously we investigated the antifeedant effect of polyguanidine on dermestid, *Attagenus smirnov*, larvae and clothes moth larvae (2). Insects had no choice of food. It was established that the antifeedant effect of polyguanidine of various molecular weights on dermestid beetle larvae was very high. Application of 2% polyguanidine solution to woolen fabric at 3 g/m² ensured reliable protection of materials from dermestid beetle (RAE = 100%). The RAE of the 2% polyguanidine solution for moth larvae was also high: 95 ± 5%. The highest protective effect of "Metacide*" upon moth larvae was achieved by using a polymer having a molecular weight of 10,000.

Along with the antifeedant effect upon keratophagous insects, polyguanidine protects natural fibre textiles and modified cellulose from deterioration by mold fungi. Its non-toxicity and complex biological effect, makes it possible to classify polyguanidine as one of compounds potentially useful for museum and restoration practice. This compound also can be used for the treatment of mounting, packaging and auxiliary materials. It can contribute to achieving more favorable biological conditions in museums.

When enumerating compounds with antifeedant effect upon dermestid beetle larvae, one cannot but mention Carboxide, a derivative of hexamethylenimine. It is known more as a repellent of blood-sucking insects and ticks. The use of 5% Carboxide solutions with an application rate of 0.3 l/m² has been recommended for practical use (3).

One of the advantages of using substances isolated from natural sources as antifeedants is their potential non-toxicity for warm-blooded animals. We studied the components of methanol extracts of lyophilized roots of red clover which had been separated by means of column chromatography on silica gel. We isolated and identified a number of secondary metabolites: isohavibetol, its ethyl ether, pseudo-baptentine and calicosine. These substances were proved to have an antifeedant effect (4). Study of a number of compounds from the pyrocachetine series, in particular clover oil showed that some components of clover oil and their derivatives also are antifeedants for dermestid larvae. It was established that

antifeedant characteristics of compounds depend on different functional substituents and double bond positions in the lateral propylene chain of the benzene ring. It was proved that isoeugenol, its methyl and ethyl ethers have a pronounced antifeedant effect. Besides that, the effect of isoeugenol methyl ether is higher than that of isoeugenol. These antifeedants for keratophagous insects that have been studied can be used widely in museum practice. Therefore, this paper offers museum specialists a range of compounds that can be used in preventive treatment. Such treatment should promote more favorable biological conditions in museums.

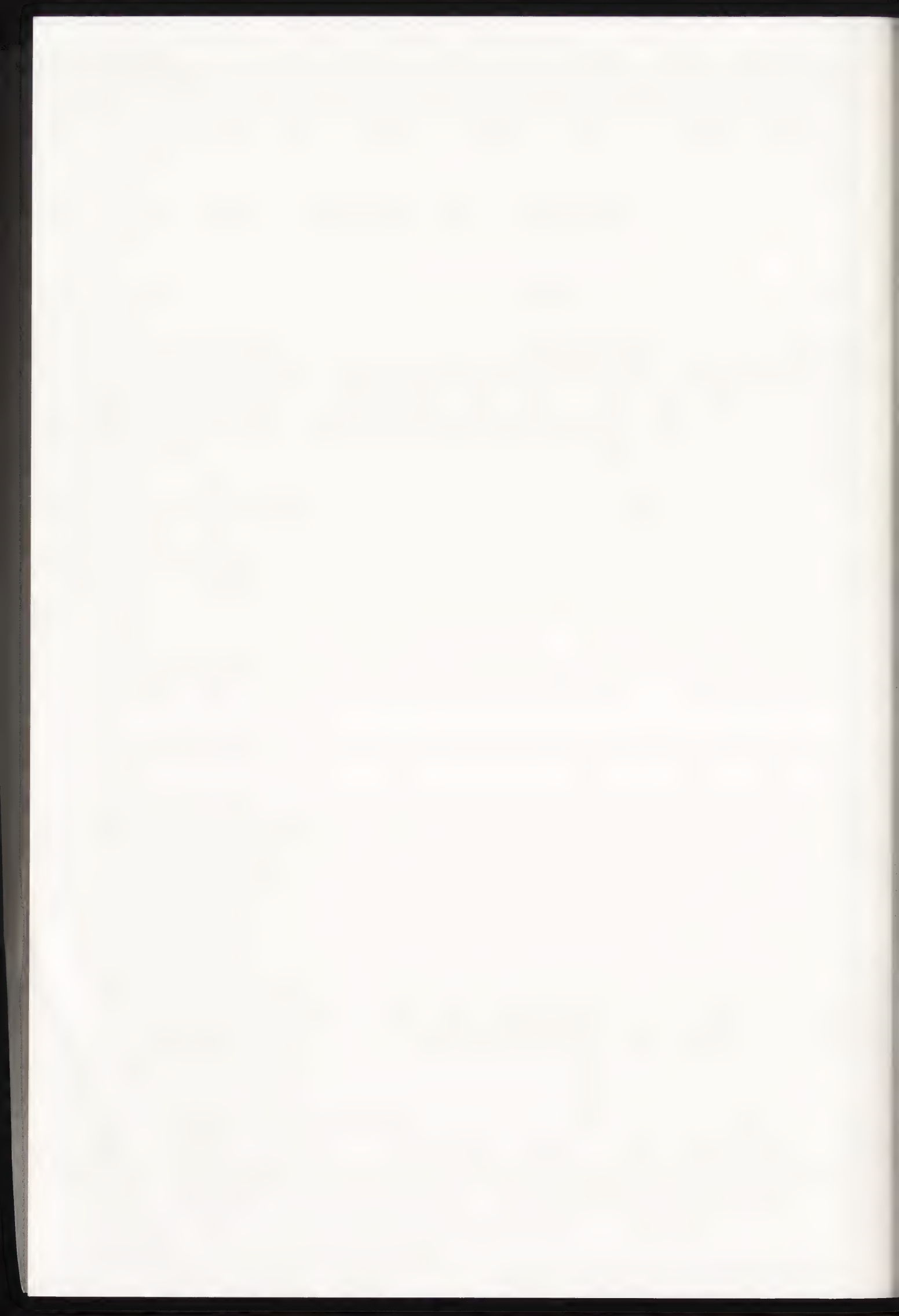
REFERENCES

1. G.A.Zaitseva, "Protection of museum textiles and leather against the dermestid beetle (Coleoptera, Dermistidae) by means of antifeedants", Studies in Conservation 32, No. 4 (1987): 176-180.
2. G.A.Zaitseva, I.N.Provorova, N.L.Rebrikova, "The perspectives of using polyguanidine for protection of museum textile against biodeterioration", in Investigation, conservation and restoration of museum textiles, Theses of reports 5th-8th of April 1988, Moscow: 15-8.
3. G.A.Zaitseva "Protection of museum textiles", 179.
4. G.A.Zaitseva, P.D. Fraishtat "Modes of Protections of textile against dermestid larvae with pyrocatechol compounds", in Investigation, conservation and restoration of museum textiles, Theses of reports 5th-8th of April 1988, Moscow: 18-20.

Working Group 26

Furniture

Meubles



THE CONSERVATION OF TWO PIECES OF BOULLE MARQUETRY FURNITURE IN THE COLLECTION OF THE J. PAUL GETTY MUSEUM

ABSTRACT

Two recent treatments on pieces of furniture veneered in Boulle Marquetry illustrate a variety of recently developed techniques for the conservation of this complex medium. Conserving a table involved replacement of losses to a complex motif in peinture en bois made of a variety of exotic veneers. After copying the pattern on Mylar, the techniques originally used for cutting of the marquetry were utilized to ensure that the replacement was not only accurate, but sympathetic. The finish combined French polishing techniques used with a nitrocellulose lacquer to prevent tarnishing of the metal inlays. The marquetry panels on a secrtaire by Montigny were lifted by applying wet surgical cotton to soften the glue, facing the marquetry with Mylar applied with 40% B72, and then working a spatula between the marquetry and the carcass. Losses to the marquetry were then filled piece by piece and the carcass was consolidated. Before relaying it, the marquetry was flattened on its face by pressing with a cork backing so that differences in thickness would be absorbed on the reverse. A mastic of sawdust, glue and black pigment was then applied between the marquetry and the carcass.

KEYWORDS

Conservation, Boulle Marquetry, Recreation of Losses, Lifting and Relaying

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INTRODUCTION

This paper is an account of the conservation of a Boulle table and a Montigny secrtaire. These treatments were interesting because they displayed examples of marquetry cutting techniques, methods of mounting it on a carcass, and restoration measures adopted centuries later. The materials composing the marquetry were equally diverse, for while the secrtaire was principally decorated with marquetry of tortoiseshell, brass and pewter, the table combined those materials with peinture en bois cut from veneers of horn, stained bone, walnut, ebony, several boxwoods, rosewood, two types of sycamore, holly, olivewood, pearwood, and service wood (Figs. 1 and 2).

The table suffered from lifting marquetry, but more importantly, it had extensive losses to the marquetry of brass, pewter and horn on the edges of the legs. The most challenging part of the treatment, however, was the replacement of a previous restoration to a large section of one of the legs which was so out of character that we (the conservators and curator) decided to replace it (Fig. 3). The secrtaire had fewer losses, but with marquetry panels that were lifting so badly that they needed to be removed completely and relaid (Fig. 2). In both cases, the success of the treatments depended on combining an in-depth understanding of the techniques originally used to execute the objects with some sophisticated conservation techniques.

TREATMENT OF THE TABLE

The treatment of the table began with the removal of a discolored varnish. The putty which had been used to fill the losses on the legs was then excavated mechanically and original loose elements were lifted off and carefully reset in their proper order (Fig. 4). Many pieces, however, were left in place to preserve their original alignment. They were simply consolidated with fresh fish glue.

To reproduce the piastre marquetry, a tracing was first made of the original on triacetate film. A photocopy of the tracing was then extended by the width of a saw kerf for each element and perforated with an instrument resem-



Fig. 3 Detail of the previously restored leg.



Fig. 1 Table (L), attributed to Andre-Charles Boulle, French (Paris); c. 1670-80; Malibu, J. Paul Getty Museum; Acc. #83.DA.22.

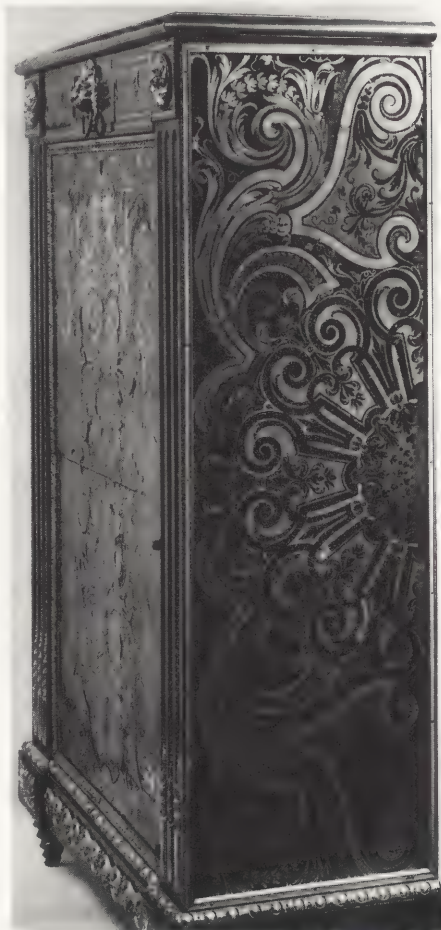


Fig. 2 Secrtaire (R), by Philippe-Claude Montigny, French (Paris); c. 1765-70; Malibu, J. Paul Getty Museum; Acc. #85.DA.378.



Fig. 4 Detail of the piastre motif marquetry on the side of one of the legs before conservation.



Fig. 5 The tracing is perforated with a needle to make a pounce pattern.



Fig. 6 Detail of the new block of oak which replaced the unsuccessful previous restoration.

bling a sewing machine on a flexible cable (Fig. 5). From this, a pounce pattern was made and glued onto a stack of the three marquetry elements: brass, pewter and horn. The marqueteur then cut along the pattern, simultaneously cutting elements in all three materials. When the stack was separated, the elements were reassembled according to the original pattern; this is the basic technique of "boule marquetry." Not only did the conservators have to copy the original marqueteur precisely, but they had to interject steps in order to reproduce bands of marquetry that would blend unobtrusively with the original. Bruno Caperon, who did this work in the atelier of Michel Jamet, also spent many hours imitating the idiosyncracies of the original marqueteur's hand. He had to use a saw blade of the same size and make his turns in precisely the same way.

The strips of piastre marquetry were mounted on glass so that the back painting, as it showed through the horn, could be color matched to the original. It was then backed with paper, as was the original, to prevent the grain of the carcass wood from showing through the horn. It also serves to isolate the marquetry from the carcass so that the two can expand and contract independently. In order to mount the replacement marquetry on the leg, a special caul was improvised which would hold the marquetry in the desired arc while allowing for the same variations and irregularities that give the original its charm. He lined the caul with first a layer of hard cardboard, then a layer of rubber, and next to the marquetry, a thin sheet of lead. Usually, brass is used, but the softness of the lead allowed for the variations to remain visible.

Having consolidated the legs and replaced the losses, the focus turned to replacing the unsuccessful restoration of one of the legs. This previous restoration was removed and care was taken to replace it with a piece of oak with the same warp as the original part of the leg (Fig. 6). As with the piastre motif, the first step in reproducing the marquetry was to make a tracing from the other legs (Fig. 7). A comparison revealed that the central volutes had been cut from the same pattern, but that the flowers around the edges were different on each leg. The conservators, therefore, copied the volute directly and selected a representative composition of the flowers from the original legs for the reproduction marquetry. This procedure was the same as the one used for the piastre motif: a pattern was glued to a stack of composite veneers. It was then sawed on a marquetry donkey, separated and reassembled according to the original color scheme (Fig. 8). A thin piece of cardboard was inserted in the stack to serve as a pattern for cutting out the ebony background. The replacement veneers were carefully color matched to the original using old veneers whenever possible. The bone was soaked in carmine indigo dye to permeate its thickness rather than staining the surface.

After assembling the individual pieces, the composition was pressed face down on an aluminum caul so that any differences in thickness would occur on the underside. The thickness was then corrected so that it was the same as the original. Next, a tracing was made of the profile of the original marquetry; this was transferred to the new piece and the joint between the two was cut. The new piece was then glued into place with hot nerve and bone glue (Fig. 9).

With the restoration of the losses completed, the conservators carefully checked the original marquetry on the remaining surfaces of the table, holding loose pieces in place with tape and regluing them with hot glue and a caul. Structural regluing was then done on the stretcher.

The next step was to treat the concave moulding of tortoiseshell and pewter that surrounded the top. Unfortunately, the glue underneath the marquetry was completely crystallized and would yield to the slightest pressure. The conservator devised a technique for lifting and relining the marquetry while preserving the original backing as original evidence. To lift the marquetry, he laid down a sheet of gauze and coated it with the synthetic resin Acryloid B72. He then slid a long knife under the marquetry. It detached, and was immediately undercoated with a fresh mastic of glue and red pigment and relined with new paper. The organic mastic, which remained on the oak carcass, was then consolidated with fresh glue. The marquetry was reglued in place with a thin mastic of sawdust and glue sandwiched between the new lining and the original to compensate for any irregularities in the surface.

The inset top was the only part not to undergo a thorough treatment. As has already been said, the top's origin remains a mystery. Although it is of very high quality, it does not appear to be original to the base. In fact, all of its elements do not appear to be contemporary and there are inconsistencies in the pattern. If the fills of a previous restoration had been excavated, the patterns on either side could not be logically connected, as they were of slightly different designs. It was therefore decided not to undertake an in-depth restoration of this panel, but simply to inpaint the fills.

Only the application of the finish then remained to be done. The entire surface was first cleaned with a plastic scouring pad moistened with water. This removed any lingering traces of glue as well as surface dirt. The peinture en bois was then sealed with a light coat of shellac and the grain was filled in the traditional manner with pumice and alcohol. A final French polish was then applied. For the "boule" marquetry, a nitrocellulose varnish was



Fig. 7 Tracing of the motif of the marquetry on the face of the leg.



Fig. 8 Detail showing the assembly of the individual pieces of the marquetry.

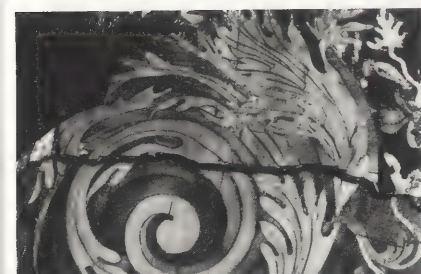


Fig. 9 Detail showing the inlaying of the new marquetry onto the leg.

applied to prevent oxidation of the metal. This was "French polished" with a pad and the varnish was then worked into the joints with solvent in order to fill them. In this way a uniform surface was achieved without a thick buildup. The gloss of the varnish was then cut back using fine steel wool, pumice and finally *Venise tripoli* on a surgical cotton pad. The entire surface was then waxed and buffed (Fig. 10).

TREATMENT OF THE *SECRETAIRE*

The conservation of the *secretaire* was very different from that of the table, but no less interesting. Instead of replacing large losses to marquetry, the conservator, Anna Østrup, was faced with lifting, restoring, and relaying four large panels of late 17th century "boulle" marquetry. Many of the brass and pewter elements were badly buckled. Although it had been decided that all four panels would have to be lifted and relaid, the buckled metal elements were first lifted individually, flattened and put back in place. The larger losses to the metal were then replaced by taking a rubbing of the losses and using it as a pattern. These steps were taken to obtain a flat, solid surface that could be stabilized during the lifting and restoration of the marquetry.

To lift the marquetry panels, the glue was first softened by applying compresses of surgical cotton soaked with water. The compresses were left on overnight and were covered with Mylar to prevent the evaporation of the water. In addition to breaking down the glue, this soaking facilitated the lifting by making the tortoiseshell more supple. The cotton was then removed and two layers of japan paper were laid down and coated with a 40% mixture of B72 in toluene. This facing held the marquetry together, since B72 will not dissolve in either the water or the alcohol, which were later injected to further dissolve the glue.

The marquetry was then separated from the ground using long knives and spatulas with injections of hot water and alcohol (as necessary) to break down the old glue (Fig. 11). As the lifting progressed, a sheet of Mylar was slid in between the marquetry and the carcass to prevent a readhesion (Fig. 12). Occasionally a piece failed to respond, so it was left on the carcass and lifted individually afterwards. When the entire panel had been separated from the support, a sheet of stiff cork was slipped under the Mylar and a piece of plywood faced with Mylar was put on the top. The panel, sandwiched between these supporting layers, was lifted off.

Having been removed from its support, the panel had to be meticulously cleaned so that it could be flattened in a veneer press. The slightest piece of hard glue caught between the marquetry and the caul would have left a pronounced dent in the surface. First the back of the panel was carefully cleaned with a scalpel and hot water. It was then lined with a sheet of triacetate held in place with B72. The panel was reversed and the japan paper was removed from the face. It in turn was cleaned in the same manner. At this point, the lifting had been completed and the panel was flattened in the veneer press; this process was repeated on the three other panels.

One of the many interesting aspects of lifting marquetry is that one could immediately see all of the previous restorations. The metal elements are always scored on the underside to improve adhesion, so a comparison of the types of scoring reveals the restorations. Ms. Østrup made a chart of the panels showing the original parts and their restorations.

With the marquetry panels cleaned and laid flat on a triacetate backing, the shellac fills were excavated and replaced where necessary with new pieces of shell. The missing stems of the flowers were replaced by sizing pewter wire and tapping it into the slots. The nail holes left in the metal parts by previous restorations were filled using a good technique devised by Michel Jamet. First the hole was reamed out using a tapered nail; the bottom of the hole was then chamfered from the opposite side. A tapered pin was driven tight into the hole, cut flush and, from the chamfered side, it was peened. The plug therefore was force fit from both sides and could not work loose. The panels were then thoroughly cleaned again to insure good adhesion once they were remounted on the carcass.

Of nearly equal interest to a lifted marquetry is the support upon which it was laid. In the case of the *secretaire*, one could see from the framing and the grain of the wood that both the front and the side panels of marquetry were still mounted on their original 17th century support panels. The front panels were mounted on a solid panel with end cleats that had been sawed in half. The support panel for the sides each had one half of a butterfly dovetail set into the back edge, proving that the two sides had once been joined together as one panel, which the design of the marquetry certainly proves. Montigny's unusual way of mounting the panels into the carcass of the *secretaire* was also discovered. Rather than cutting a tongue on the edge of the panels that would be framed by grooves in the carcass, he planed a rebate on the underside of the four edges (Fig. 13). The tool marks strongly suggest that he then chiselled out corresponding rebates on a carcass that had already been assembled and then simply set the side panels into the carcass frame.



Fig. 10 The table after conservation.



Fig. 11 The side of the secr-taire overlaid with japan paper and consolidated with B72. The conservator is working the marquetry loose with long spatulas and injecting alcohol to dissolve the glue when necessary.



Fig. 12 As the marquetry is detached, a sheet of Mylar is inserted between the carcass and the marquetry to prevent readhesion.

The uncovering of the substrate was not only interesting, but it was of great importance for thorough conservation of panels in this condition. It would have been shortsighted to lift a panel of marquetry, restore it, and relay it on a ground that had splits along the grain and uneven surfaces between the framing members. These problems would prevent the marquetry from lying flat and the splits would soon occur in it as well.

After first removing the original mastic of glue and pigment with which the marquetry had been backed, the conservator completely disassembled all of the support panels. They were then cleaned and reglued with strips of oak inset to compensate for shrinkage that had created gaps. Far more difficult, however, was trying to flatten the badly cupped panels. Marquetry relaid on warped boards would give a noticeably wavy appearance. The boards were partially flattened using the traditional technique of humidifying the concave side face down while drying the convex side with heat. To compensate for the rest of the cupping, slices of oak veneer were laid in the recesses and smoothed out with glue mastic.

Having conserved the individual components, the process of remounting the marquetry on the substrate was begun. The marquetry panels were first glued face down on kraft paper mounted on zinc plates. They were then pressed from behind with cork lined cauls so that the face of the marquetry would be flat and any unevenness in thickness occurring on the back. The underside of the metal elements were then given a final cleaning with pumice rubbed with a cork to degrease and ensure good adhesion. They were then painted with a mixture of fish glue and smoke black pigment. Several more coats of this mixture thickened with sawdust were applied and, after setting up, were levelled up with a tooothing plane.

The support panels were coated with the glue and pigment mixture and the marquetry panels were put in place and kept in the veneer press for five days. Each of the panels was then remounted on the carcass and the ebony framing veneer was relaid, with strips occasionally being added to compensate for shrinkage.

A finish of nitrocellulose lacquer "French polish" into the joints was applied, cut back with fine abrasives, and waxed.

It can be seen from the description of these treatments that they brought to bear the full range of marquetry conservation techniques. The two objects were extremely rich in materials and varied in their problems. For this reason, the two treatments, which were done concurrently, serve as an excellent model of the marriage of history, tradition, and modern conservation science. The conservators had to assimilate the techniques of the original artists and then conserve the work without imposing their own personalities.

¹ In English, "painting on wood" describes the representation of three dimensional compositions using wood veneers of many colors and sand shading to create the illusion of depth.



Fig. 13 A drawing showing the joining of the carcass underneath the marquetry.

ABSTRACT

THE USE OF FLUORESCENT MICROSCOPY IN FURNITURE CONSERVATION

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Introduction

Fluorescence microscopy has been used in biological studies since the first part of this century. It is now commonly used in immunology and histology. The application of this method to art conservation is relatively recent. The primary value of fluorescence microscopy is to allow the viewer to observe and characterize materials present in coatings that otherwise lack visual definition or distinguishing characteristics.

Literature Review

The use of fluorescence microscopy in art conservation was presented in "The Use of Direct Reactive Fluorescent Dyes for the Characterization of Binding Media in Cross Sectional Examinations"² by Richard Wolbers and Gregory Landrey which focuses on the use of fluorochromes to identify specific characteristics of components in a surface coating. Publications on the development of binding media identification is reviewed. Mechthild Baumeister published "Historic Lacquers and Polishes on Furniture, Fluorescent Microscopy as a Method of the Examination of Historic Furniture Finishes" in 1988.³ Baumeister presents a variety of case studies showing how finish layers can be identified by this method. Numerous publications on the subject are cited and discussed in this article. The increased application of fluorescence microscopy is evident by numerous references to it in recent articles and professional papers.

Equipment and Materials

Most fluorescence microscopes operate in a similar manner. An ultraviolet light generated from a high pressure mercury bulb, a xenon bulb or in some cases a halogen bulb, is directed through an excitation filter, then passed on to a dichroic mirror which illuminates the specimen with an ultraviolet light beam. Specimens capable of fluorescing emit light up the microscope tube to a barrier filter which passes the useful bands of fluorescence to the objectives of the microscope. Many of the components found in finish layers are capable of primary or auto fluorescence, rendering them clearly visible when irradiated with ultraviolet light. Often these materials are difficult or impossible to see under normal light microscopy but have identifiable characteristic auto fluorescent colors.

The primary piece of equipment used in the Winterthur Laboratory is a Nikon Labophot Biological Microscope with an Episcopic-Fluorescence attachment which uses a 100 watt high pressure mercury lamp. This was chosen as it offered to be a good balance between optic quality, durability and economy. The microscope is equipped with two "filter blocks," which are Nikon's violet-2B and Blue-2A cubes.⁴ The fluorescence system in use at Winterthur is augmented with a Intralux 6000 halogen light source directed toward the specimen with fiber optics. This allows the viewer to study the specimen under ultraviolet light, normal light, and a combination of the two.

Auxiliary components have been added to help visualize and record the information. A Nikon photomicrographic attachment, Microflex HFX-II, is used for photography. A Hitachi FP-C1H color camera coupled with a Sony 13" monitor is used so that the sections under study can be viewed by two or more people. The Hitachi camera is particularly good at reproducing the low light level color encountered with fluorescence microscopy. As an alternative to recording information on photographic film, Sony MVR-5500A and Kodak SV7400 still video recorders are used to store the image on a 3½" floppy disc. Text

¹Brief overviews can be found in Eberhard Becker, Fluorescence Microscopy (West Germany: Leitz, 1985) and H.M. Holz, Worthwhile Facts about Fluorescence Microscopy (Oberkochen, West Germany: Zeiss, 1985). Both of these publications are recommended as introductions to the subject.

²Richard Wolbers and Gregory Landrey, "The Use of Direct Reactive Fluorescent Dyes for the Characterization of Binding Media in Cross Sectional Examinations," AIC Preprints 1987 (1987) 168-202.

³Mechthild Baumeister, "Historic Lacquers and Polishes on Furniture, Fluorescence Microscopy as a Method of Examination of Historic Furniture Finishes," Restauero (April, 1988) 100-104.

⁴The following Spectral transmissions are published in the Nikon Episcopic-Fluorescence manual. Block V-2A: Excitation, 380-425; Dichroic Mirror, 430; Barrier Filter, 450 (Nm). Block B-2A: Excitation, 450-490; Dichroic Mirror, 510; Barrier Filter, 520 (Nm).

Surface coatings in furniture are fundamental to the aesthetic and historic value of an object. Conservators strive to understand and preserve these coatings in the course of their work. Fluorescence microscopy is a significant practical aid in characterizing transparent, translucent and opaque coatings on furniture. This allows for a higher degree of accuracy in evaluating, treating and representing furniture. A microscope with an epifluorescence attachment has been in use in Winterthur's furniture conservation laboratory for three years. A selective review of the several thousand samples studied since 1986 represents substantial progress in the conservator's ability to understand and care for historic surface coatings on furniture.

KEYWORDS

Fluorescence Microscopy,
Furniture Conservation.

is put onto the disks with a FOR-A VTW-100 video typewriter. This recording system allows for immediate image recording or retrieval and the possibility of image processing.

Reactive fluorescent dyes (RFDs) or fluorochromes are used regularly in fluorescence microscopy. The application and use of fluorochromes is covered extensively in the literature previously mentioned and in published materials from the various fluorescence microscope manufacturers. The RFDs used most often in our fluorescence microscopy are fluorescein isothiocyanate (FITC) in acetone for protein and Rhodamine B in ethanol for lipids.⁵ Of these two, Rhodamine B for lipids is the most commonly employed.

Sample Preparation

Extraction of a sample is a destructive procedure which requires careful consideration and assessment of the amount of information which will be gained from the cross section.⁶ Samples are taken with a surgical scalpel or a "Beaver" blade.⁷ The difficult aspects of sample taking include choosing the location, taking as small an amount as possible, extracting substrate material along with the surface coating and keeping the full stratification intact. Using a stereo microscope in the sampling process can minimize these problems.

Many factors enter into the choice of location. An area representative of the entire surface should be selected. Areas adjacent to a join or a split are sometimes ideal for sample removal. Large objects such as a high chest may require several samples so a more complete finish history is provided.

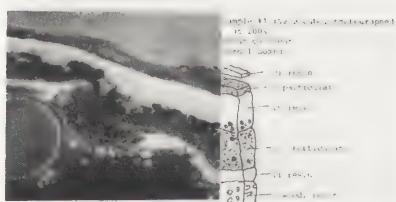
The finish sample is removed from the object, cast in a hard, clear resin using a small mold and ground and polished perpendicular to the plane of the surface being examined. The polishing is done by hand, using a 600 grade silicone carbide sandpaper, followed by a .1 micron micro-alumina. This process produces a microscope ready cross section.⁸

Case Studies

Case Study I

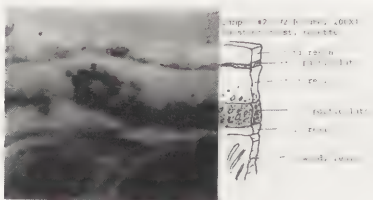
Chest on Chest, Philadelphia, Pennsylvania, ca. 1765
Maker unknown⁹

This chest on chest was scheduled for surface coating characterization with two purposes in mind, first, to differentiate between original and restored ornamentation and second, to assist in designing a cleaning system to reduce the opaque and sticky nature of the finish.



Sample #1
Scroll Board

As an integral part of the core structure of the chest on chest, the scroll board's finish was chosen as a benchmark to match with surface histories from other parts of the chest on chest. This sample was taken from a protected area of the scroll board near the applied carving. The six finish layers found here form a unique stratification that is a result of many years of finish and polish being added to the coating below. The pattern defined by this layering was then compared to sample #s 2 and 3 with differing results.



Sample #2
Rosette

For many years, there has been a strong desire to determine with a higher degree of accuracy the originality of the two rosettes on the terminus of the "broken arches" of the upper case of the high chest. The cross sections from both rosettes represented by sample #2 match the finish layering found in sample #1. These results give credibility to the originality of the rosettes.

⁵ These reactive fluorescent dyes are available through Sigma Chemical Company, P.O. Box 14508, St. Louis, MO 63178, USA. Rhodamine B for Lipids catalog #R4252; Fluorescein Isothiocyanate for protein, catalog #F7250.

⁶ A primary reference for the extraction of surface coating samples from works of art is Joyce Plesters, "Cross Sections and Chemical Analysis of Paint Samples," Studies in Conservation (April, 1956).

⁷ These are small yet sturdy blades manufactured by Beaver, Waltham, MA 02154, USA.

⁸ "Bio Plastic," a polyester resin is used as a sample casting medium. Ward's Natural Science Establishment, Inc., Rochester, NY, USA. Item #0351720.

⁹ See Joseph Downs, American Furniture, Queen Anne and Chippendale Periods (New York: MacMillan, 1952) pl. 184. See also Charles Hummel, A Winterthur Guide to American Chippendale Furniture (New York: Crown, 1976), p. 84. Scott Friedgen-Veitch and Nancy Reinhold participated in the microscopy and carried out the treatment discussed in this case study.

Additional technical and stylistic information supports this finding.

Sample #3
Cartouche

This section is markedly different than that found on #1 and #2 suggesting that either the cartouche is a later addition or that it was refinished. It is improbable that an old finish on the cartouche could be so thoroughly removed as to eliminate all traces of earlier coatings. Cross sections from furniture that are known to have been refinished, commonly show earlier resins still imbedded in the wood. It also unlikely that the cartouche was completely refinished while the rest of the chest was left unscathed. The most compelling reason for such a markedly different and singular finish history on the cartouche is that this piece of ornamentation was replaced.

Sample #4
Drawer front, before treatment

The use of fluorochrome, Rhodamine B (.125% in ethanol) for lipids is used on this sample to highlight a thin oil layer on top of a spirit varnish. The oil containing components of the finish are fluorescing a bright orange red as a result of reacting with the fluorochrome. This oil layer is presumed to be the disfiguring component of the finish layer. Evidence of oil is also found in the wood under existing surface coatings.

Sample #5
Drawer front, after treatment

The observations noted under sample #4 indicated that an oil specific cleaning system would delete the disfiguring layer while not disturbing the spirit varnish immediately beneath it. An enzyme and detergent gel was applied to the surface of the chest on chest which successfully broke down the oil layer, allowing for its removal.¹⁰ The finish was cleared with stoddard solvent followed by a carnauba and beeswax coating which was buffed out to an appropriate sheen. The effect of the cleaning system can be observed in sample #5. The oil layer is no longer present while the remaining finish zones are intact. Fluorescence microscopy proved useful here in helping to measure the effectiveness of the treatment and its impact on the object.

Case Study II

Painted Card Table, Baltimore, Maryland, ca. 1810
Attributed to John Finlay¹¹

Sample #6
Photographed at 200X magnification
Apron

This table was brought to the furniture conservation lab because of a dark and disfigured surface hiding an original paint scheme below. The objective of the treatment was to clean off the offending layer without disturbing the original paint and varnish scheme below. Cross section samples were taken from the table and studied using the systems described above.

The results from the microscopy were quite clear. The original surface coating stratification can be found in layers ii-vi. The paint and some gold leaf is found in layers ii-iv while v and vi are two compositionally similar clear coatings which lie on top of the paint. The first varnish layer (v) has wetted directly into the paint and gilt area while the second varnish coating (vi) has cupped and cracked in the same manner as the first. The dark line between the two varnish layers is likely to be a result of original finish processes rather than being a grime line.¹² The outer coating, layer vii, is a heterogeneous zone that contains particulate and resin which fluoresces a gray-white. A bright orange-red fluorescence in layer vii indicates a positive reaction to the fluorochrome Rhodamine B for lipids showing the presence of oil. Layer vii can be seen flowing into the cracked varnish coatings below, clearly marking it as a non-original layer.

¹⁰ The oil was cleaned from the chest on chest with an enzyme gel system. The aqueous gel included .7% Trizma (Sigma #T-5253), 1.6% Methocel (Dow Chemical, Midland, Michigan 48674, USA, 1-800-258-2436), .1% Triton (Sigma #X-100). Type VII Lipase enzyme from *Candida cylindracea* (Sigma #L-1754) was added to the gel at an approximate ratio of 50 mg to 10 ml of solution.

¹¹ See Dean Fales, Jr., *American Painted Furniture* (New York: Bonanza, 1986), p. 132. See Also Charles F. Montgomery, *American Furniture, the Federal Period* (New York: Viking Press, 1966), p. 451. Nancy Reinhold was the conservator that carried out the microscopy and treatment discussed here.

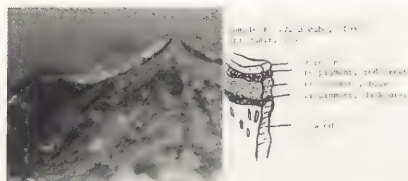
¹² Remarkably similar paint and finish histories have been found on other painted furniture of this period from Baltimore showing the same two layer varnish with a dark thin line between them. See Wolbers and Landrey.

Understanding the surface coating of this table was critical to devising and carrying out a safe cleaning system that would meet the stated objectives. An enzyme and gel system was used to clear the table of the disfiguring coating in a manner similar to the treatment discussed in case study I. This effectively uncovered the original paint and varnish coating below without disturbing the original stratification found in layers ii-vi.

Case Study III

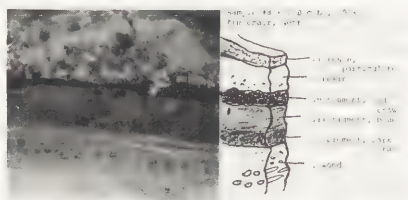
Arm Chair, Long Island, New York, ca. 1740

This chair was examined prior to its purchase by the Winterthur Museum to ensure that it was of American origin. The use of hickory for the seat was quite telling in that hickory is found almost exclusively in furniture of American origin.¹³ It became important, then, to determine the originality of the seat. Cross sections were taken from the seat and from the right rear leg looking for similar or divergent finish and paint histories.



Sample #7
Right rear leg

Five layers are visible in this sample including a primary layer of large particulate and resin, a blue coating, a red-brown zone and two resin films. The coarse, hand ground pigment bound in a natural resin found in the early or original layer (ii) is characteristic of 18th century materials and processes used in making paint for furniture. The five layer stratification observed here appears elsewhere on the body of the chair. Both samples 7 and 8 were viewed under ultraviolet light, normal light and a combination of the two.



Sample #8
Seat

This sample has the same surface coating history as the seat rail suggesting that the seat belongs to the chair and is not a replacement. This helps to affirm the significance of the identity of the hickory seat and the chair's American provenance. This information is consistent with a structural study of the chair which confirmed that the seat and rails appeared unaltered.

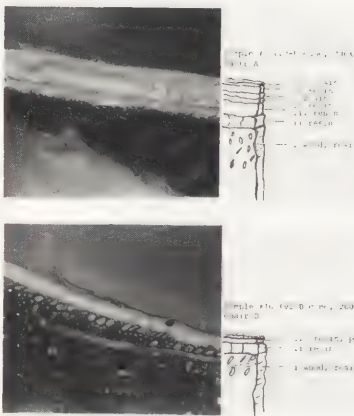
Case Study IV

Cadwalader Furniture Suite, Philadelphia, Pennsylvania, ca. 1770¹⁴

The furniture included in this study is believed to have been built for General Cadwalader in late 1770 and early 1771 by Thomas Affleck and other Philadelphia artisans. In the course of carrying out the microscopy on some of the furniture it was observed that a unique stratification existed on a "Cadwalader" side chair in the Winterthur Collection (chair A, sample 9) and on a recently discovered easy chair owned privately (chair B, sample 10). The "common thread" is the first layer which fluoresces a salmon color and is segmented, giving the cross section a brick-like appearance. This spurred us on to examine 22 surviving pieces that may have come from the Cadwalader order. Finish sections were drawn from many of these objects and compared as a group. The identical unique brick-like finish stratification found on the first two chairs mentioned was also encountered on several additional pieces (samples 11 & 12). In one case, this primary coating was found under seven aged finish layers. This suggests that this furniture is indeed connected and had an original or early coating that could be traced to the point of fabrication or first generation of ownership. This is yet another application of fluorescence microscopy by using it to gather information on a group of potentially related objects.

Samples #9-12

The first finish layer in all of these sections is a salmon color with periodic checking giving it the brick-like appearance discussed above. The color is not necessarily unique, but the nature of the checking and the location of this layer immediately next to the wood on all of the samples presents a singular example that has not been observed in any other study to date. These sections show remarkably similar traits in the first finish layer which suggests that the furniture is indeed a set and was finished originally with the same materials.



¹³ For a further discussion on hickory as an American cabinet wood, See F. Lewis Hinckley, Directory of the Historic Cabinetwoods (New York: Bonanza, 1960), p. 21-22.

¹⁴ See Philip Zimmerman "A Methodological Study in the Identification of Some Important Philadelphia Furniture," Winterthur Portfolio (Chicago: University of Chicago Press, 1978), pp. 193-208.

Case Study V

Pole Screen, Philadelphia, ca. 1770

Maker unknown

The dark and sticky nature of the finish on this piece was identified as needing treatment with the hope of making the finish lighter in color and no longer sticky while keeping the existing varnish layers intact. Microscopy was carried out to see what the nature of the finish was, and to determine if the stated objectives could be achieved.

Sample #13

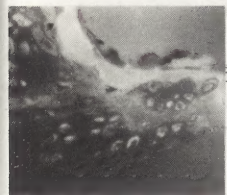
There are three zones to this finish with distinct characteristics. The first layer is a resin layer with a substantial amount of particulate, possibly pigment that has penetrated deep into the cellular tissue of the wood. The middle layer is essentially a clear resin layer. The top coating is a thin oil layer that is causing the surface to be sticky. This information indicates that while the finish can be safely cleaned, the dark nature of the finish cannot be fully reduced without complete finish removal since it is a result of the first finish layer. The finish treatment was very similar to that described in case studies I and II. However, the results were different in that the dark nature of the coating was not possible to eliminate while retaining the existing historic finish. The use of fluorescence microscopy was able to help establish the limitations of the cleaning and set realistic expectations for the treatment.

Conclusion

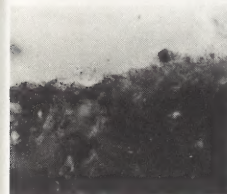
Fluorescence microscopy gives us a greater understanding of furniture finishes than has been possible before. This is of particular value as we try to base our judgements on verifiable information and measure the effect we are having in the course of our treatments. A conservator can do this work directly without having to go through other specialists. It is a relatively inexpensive way to take much of the guesswork out of evaluating and caring for historic furniture finishes. These studies have revealed a substantial amount of information lodged in the finish stratification of the objects being examined. This underscores the need to value and preserve existing surface coatings on finish of historic, artistic or cultural value.



Sample #11 (V2-B cube, 200X)
Side Chair
II resin
I wood, resin



Sample #12 (V2-B cube, 200X)
Card table
III resin, particulate
II resin
I wood



III resin
II particulate, pigment
I wood

Sample #13 (V2-B cube, 200X)
Pole screen

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